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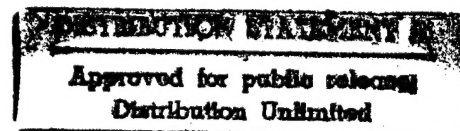
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Regional Technical Conference

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October 24, 1968

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EPOXY MOLDING COMPOUNDS CHARACTERIZATION AND CLASSIFICATION

Robert Flynn

Technical Specialist

and

A. N. Cianciarulo

Group Leader

CIBA Products Co.

Toms River, N. J.

ABSTRACT

This characterization and classification has been developed to provide a basis for further development and evaluation of raw materials in epoxy molding compounds. Typical property ranges for each class of compounds are listed to demonstrate the present state of the art and provide a basis of comparison for future development.

INTRODUCTION

Formulated molding compounds have been available for over fifteen years. During that time, there has been a continuous development in technology which has resulted in more diversified formulations to meet different types of applications. These diversified formulations are possible through the unique properties offered by the epoxy family.

In attempting to develop and evaluate new resins and hardeners for molding compounds, it is first necessary to characterize the variables encountered in molding technology and classify existing materials by some meaningful parameters. It is important to note that this classification is developed for the purpose of evaluating raw materials and should not impose any restriction on present or future formulation and performance requirements.

An epoxy resin is generally defined as any molecule containing more than one epoxy group capable of being converted to a useful thermoset form. Typical of those resins finding use in molding compound formulations are the bisphenol types and the high functionality novolac types (see Figure 1).

The conversion of an epoxy resin from a thermoplastic to a thermoset material occurs principally, through the reaction of the epoxy groups. In molding compounds, this is accomplished by the addition of hardeners which co-react with the resin and accelerators which may be used to increase the rate of reaction. Typical of hardeners used are amines, acid anhydrides and phenolic hydroxyl containing materials such as novolacs (see Figure 2).

Since each of the generic families of epoxy resins and hardeners can be supplied in different viscosity or melting point ranges, binder systems for molding compounds can be formulated to meet a wide range of elevated temperature

viscosities. This permits the development of compounds which have different mold flow capabilities and wetting characteristics. In addition, epoxy resins exhibit rapid changes in viscosity with respect to changes in temperature, permitting the formulation of systems which are solid at room temperature but still capable of low viscosities at molding temperatures. Epoxy systems are 100 per cent reactive and no by-products are generated during the cure cycle. Epoxy binder systems can be formulated to meet specific gel and cure times. When properly formulated and cured, epoxy systems possess good mechanical strength, excellent electrical properties, and good chemical resistance. These systems are also capable of relatively high deflection temperatures, low mold shrinkage, and low thermal expansion properties which reflect good dimensional tolerances.

Epoxy molding compounds are capable of undergoing an irreversible chemical reaction in relatively short periods of time when molded under heat and pressure. They are supplied as single-package systems which are engineered to meet different molding parameters and application requirements. They include formulated compounds which range from low melt, long flowing transfer molding types to highly reinforced compression molding types.

In order to evaluate new resins and hardeners for their suitability in epoxy molding compound formulations, it was necessary to assess the present state of the art. This was accomplished by the evaluation of four interrelated parameters consisting of: Formulation, fabrication, molding and application (see Figure 3).

A. Formulation

An epoxy molding compound formulation consists of two principal components which are the binder and the filler systems (see Figure 4).

The binder system contains the chemically reactive ingredients of the formulation and is capable of undergoing a reaction when exposed to heat and pressure resulting in a thermosetting product. The ultimate purpose of the binder system is to provide cured properties consistent with the application's requirement. As discussed earlier, epoxy systems permit a wide latitude of variation with respect to the generic family of resin and the curing mechanism which may be used. Often, different generic resins are combined in order to develop systems which yield modified properties or handling characteristics. For example, a bisphenol-A type resin can be combined with a high functionality epoxy novolac resin to yield a system with a compromise in functionality and cured flexibility as compared to each of the original resins. In addition, the chemical resistance of a system toward specific reagents can be influenced by the curing mechanism used. An acid anhydride hardener will offer excellent resistance to acid environments while an amine cure will offer maximum resistance to alkaline environments. The flow profile of an epoxy molding compound depends not only upon the concentration of binder system contained in the formulation or melt viscosities of the raw materials which make up the binder system, but in part, also depends upon the reactivity of the system under specific molding conditions. Reactivity or gel times are often adjusted by the addition of an accelerator. Through this single modification, different flows and cured properties can be realized.

The filler system consists of extenders and/or reinforcements of various types as well as pigments, and in some cases, internal release agents. Although the filler system is not ordinarily chemically reactive (except through surface coatings which may be present as coupling agents), it does contribute to the flow profile and ultimate cured properties of the system. The more common extenders are silicon dioxide, dolomitic materials, talcs, and other minerals usually having classified particle sizes. Extenders are added for the purpose of reducing compound cost and to yield specific cured properties, such as low shrinkage and thermal conductivity. Reinforcing fillers such as glass, asbestos, or synthetic fibers are usually added to enhance the compound's mechanical properties. In recent years, materials have been added to formulations to yield controlled specific gravities. The filler system is formulated to meet specific application requirements and, therefore, fabrication and molding parameters are usually influenced by the type of filler system involved. Highly reinforced compounds are usually intended for compression molding techniques where fiber integrity can be maintained during the molding cycle. Encapsulating grade compounds usually do not include a high degree of reinforcement, therefore, these materials can be transfer molded. The filler system may combine the extreme characteristics of an encapsulation transfer compound and a highly reinforced compression compound in order to meet compromised requirements.

B. Fabrication

Chemical and physical properties of the binder and filler systems, as well as the intended application and molding parameters, will influence fabrication technology.

Typical properties affected by fabrication are shelf life, retention of reinforcement integrity, product uniformity, and product reproducibility. Two types of finished compound formulations emerge as a result of the fabricating considerations. They are the single-component compounds in which all ingredients have lost their individual identity and integrity, and the multi-component compound which is an admixture of ingredients. The fabrication methods utilized to manufacture single-component compounds involve coating the entire filler system with the binder system. The multi-component system can be fabricated in a manner where all ingredients are reduced to a suitable particle size and mixed.

Melt, liquid, solvent, dry or combinations of these blending methods are used to fabricate either single or multi-component systems. These blending methods are defined as follows:

1. Melt Blend

A process using heat to melt one or more solid ingredients to form a single-component molding compound or a formulated ingredient.

2. Liquid Blend

A process using one or more ingredients which are liquid at room temperature to form a single-component molding

compound or a formulated ingredient.

3. Solvent Blend

A process using one or more solvents in combination with the binder to form a varnish solution.

4. Dry Blend

A process using solid ingredients admixed so as to maintain their individual characteristics.

Solid ingredients are most suitable for the melt blend process. This fabricating approach requires that the resin and hardener system be capable of melting in order to incorporate fillers. Since heat is associated with this process, the extent of binder advancement will depend upon the reactivity of the ingredients (see Figure 5).

A liquid blend fabricating process is capable of utilizing liquid resins and hardeners in binder systems. Since the ingredients are in liquid form at room temperature, a minimum of heat is required to reduce their viscosity. Filler can then be incorporated and wet-out at relatively low process temperatures. However, if a grindable compound is desired, the total system must be advanced ("B"-staged). This requires that the resin and hardener be capable of undergoing predictable partial reaction under controlled process conditions (see Figure 6).

A wide range of liquid or solid resins and hardeners can be used in the solvent blend process. This process involves dissolving the binder system in a suitable solvent to yield a varnish solution. A filler system (extender and/or reinforcement) is then wet-out by the varnish solution, and the solvent, subsequently, removed under elevated temperature. This requires that the binder system be capable of minimum advancement under the necessary solvent evaporation process (see Figure 7).

A dry blend fabrication process involves the admixing of coarse ground ingredients. The total mix is then reduced in particle size so as to yield a macroscopic homogeneous blended powder. Variation of this process can involve first coating parts of the filler with resin and part with hardener by the melt blend or solvent blend process. The coated components are then admixed in the appropriate ratio and the mix is reduced in particle size to a macroscopic homogeneous powder. In either case, the pulverized powder is then densified, ground, and classified to a suitable particle size distribution (see Figure 8).

C. Molding

Epoxy molding compounds are supplied in a variety of densities (bulk factors) which are a function of formulation and fabrication. The bulk factors may range from 1.5 to greater than 15. These values are usually reduced by mechanically or hydraulically pre-forming the material into appropriate sizes and shapes. This facilitates material handling, preheating, and mold loading. Pre-

heating is required in most cases in order to ensure uniform material flow and cure.

The primary molding techniques employed with epoxy molding compounds are compression and transfer molding. During compression molding, the lower section of the mold is charged with a material which is then formed under heat and pressure by forcing in the upper section (see Figure 9).

Transfer molding involves the transfer of molten compound under heat and pressure from a pot through a series of runners and gates to a cavity (see Figure 10).

Compression molding uses materials containing high reinforcement to produce structural parts. By displacement methods, the reinforcement integrity is maintained.

Transfer molding, on the other hand, depends on good flow properties and generally involves materials with small particle size filler systems. This molding technique is utilized where structural requirements are comparatively low and high rates of production desired.

The performance of a compound will greatly depend upon the mold design as well as the molding technique. Compounds are engineered not only for their cured properties but also for their behavior under specific molding parameters.

D. Application

These are arbitrarily divided into four general classes which are:

1. Electrical encapsulation application
2. Electrical and/or chemical structural application
3. Structural application
4. Special application

Each class imposes its own material requirement which can be met through the coordination of proper formulating, fabricating and molding considerations.

1. Electrical encapsulation application

The molding characteristics of epoxy transfer molding systems make them highly suitable for the encapsulation of electrical components. Epoxy compounds can be used in molding reliable components at high production rates and low cost. This technique is often replacing such technology as potting, casting and fluidized bed coating, particularly where improved dimensional tolerances and higher production rates are required. Electrical encapsulation includes small electronic and larger electrical components.

Typical of the small electronic component is a semi-conductor where a high degree of material purity and process control is required. The molds utilized to encapsulate

semi-conductors may be designed with as many as fifty or more cavities. This requires that the compound have a low melt viscosity coupled with suitable gel time to enable long flow at low molding pressure.

Representative of larger electrical components are coils. Although this application does not require electrical properties as good as needed for semi-conductors, encapsulated coils do require compounds which exhibit higher cured mechanical properties. The molds utilized in the encapsulation of coils do not include a large number of cavities. However, good flow is still required due to the volume of material that must be transferred to encapsulate the larger coil insert. In addition, low melt viscosity systems are necessary to permit the transfer of the material at low pressures in order to prevent distortion of the insert during the molding cycle.

2. Electrical and/or chemical structural application

Characteristic components are associated with an electrical and/or chemical application requiring some structural integrity. Transfer and compression are both applicable as molding techniques. Components for this application may be small or large.

Examples of small components are: connectors, bobbins, potting cases, pump impellers, etc. These components require some mechanical strength coupled with good electrical and/or chemical properties. Whenever possible, transfer molding techniques are used to realize higher production rates.

For larger parts, such as pipe fittings, switchgear, etc., where higher strength is needed, compression molding is utilized.

For this application, higher molding pressures can be tolerated since sensitive inserts are not generally involved as part of this molding operation. Therefore, flow capability may be sacrificed for increased reinforcement.

3. Structural application

Typical of this application are molded components such as: pipe fittings, textile spinning buckets, pump housings, impellers, etc. The major requirement imposed is high mechanical strength which may be coupled with good electrical or chemical properties. Materials which meet these needs are highly reinforced systems and, as a result, usually dictate compression molding techniques in order to retain the integrity of the reinforcement during the molding cycle. Structural components may vary in shot weight from 50 grams or less to more than 5,000 grams per shot.

4. Special application

Included within this area are applications which involve a specialized property or performance requirement not previously covered. Examples of these include: specific gravity for aerospace, marine or ballistic applications, wear characteristics for bushing or gear applications, and electrical or magnetic properties for microwave guides or communication systems. Materials utilized for these applications vary greatly in formulation and cannot be specifically characterized because of the diverse requirements.

CLASSIFICATION

Two considerations emerge as a result of the evaluation of formulation, fabrication, molding and application characterizations. These are: flow capability and reinforcement. This classification of epoxy molding compounds is based on these two criteria and is divided into four broad basic grades of material.

A. Type I - Encapsulating Transfer Grade

This classification includes compounds which are designed for high flow and low pressure. Formulations of this type have binder systems with a low melt viscosity at molding temperatures. In addition, they include filler systems which are unreinforced and enable material flow at relatively low pressures through small gates into multi-cavity molds. Fabricating techniques are employed which yield free flowing, multi-component or single-component powders or granular compounds capable of being preformed. The Type I materials are utilized primarily in electronic and electrical applications. Therefore, they should have good barrier protection and good electrical properties for encapsulated components when exposed to adverse environments. Systems with a high degree of chemical purity in both the binder and filler components are required. Also, these materials should have reliable flow properties in order to meet the highly sensitive encapsulating molding parameters.

B. Type II - High Pressure Transfer/Low Pressure Compression Grade

Representative of this type are materials where flow can be sacrificed for reinforcement addition. Although compounds of this type may be utilized for components associated with electrical and/or chemical applications, they are not usually intended as encapsulating materials. Therefore, the high degree of formulation purity imposed on Type I materials is not required. In addition, since varying degrees of structural integrity are associated with this type, different amounts of reinforcement are incorporated. The fabrication parameters are adjusted so as to permit retention of the structural capability of the system. For applications requiring a minimum degree of reinforcement, systems are engineered to permit transfer molding at higher pressures and usually through larger gates than encountered with Type I materials. When a higher degree of reinforcement is necessary, then compression molding techniques are utilized.

C. Type III - Compression Molding Grade

Materials of this type are designed primarily for applications requiring superior mechanical properties and, as such, are high pressure compression molding compounds. The usual means of obtaining high structural strength is by reinforcement with long glass fiber. This necessitates using compression molding techniques. Fabricating parameters for this type of material include premix as well as chopped prepreg technology. These Type III compounds are usually supplied in a fibrous form capable of preforming for purposes of handling and mold loading.

D. Type IV - Miscellaneous Grade

Simply stated, this type includes any system not included under Types I, II and III and which are formulated for special applications.

TYPICAL PROPERTY RANGE

In an attempt to indicate the present state of the art, commercially available formulations were classified according to the supplier's application and molding recommendations. The supplier's reported physical data for each material was then compiled and a range tabulated for the listed properties. Figure 11 lists the results of the compilation. A property range for Type IV materials has not been included since the diversification of special applications does not lend itself to a practical property range.

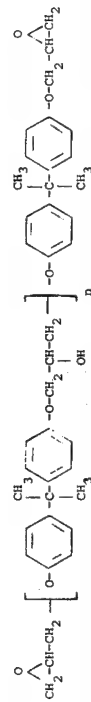
REFERENCES

1. Flynn, R. and Luker, H.C., Epoxy Resins, Modern Plastics Encyclopedia, 1968.
2. Lee, H. and Neville, K., Handbook of Epoxy Resins, McGraw-Hill Book Co., 1967.

OXIRANE RING
(Epoxy Group)



General Structure of a Bisphenol-A Type Resin: "n" designates the number of repeating units



General Structure of O-Cresol Novolac Type Resin: "n" designates the number of repeating units

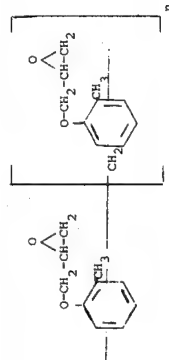


FIGURE 1 Typical epoxy resins used in molding compound formulations

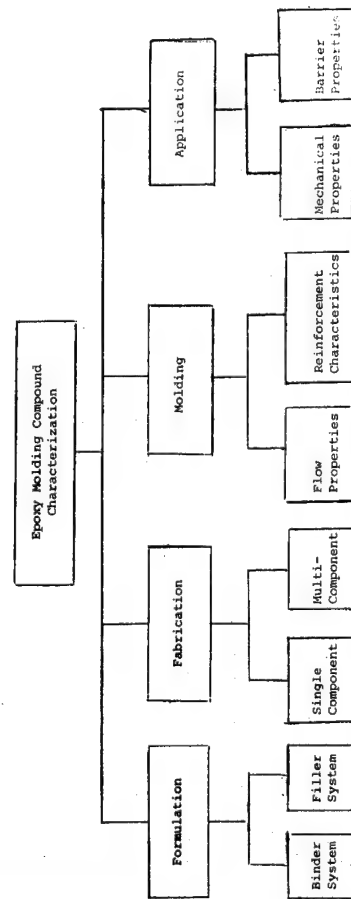
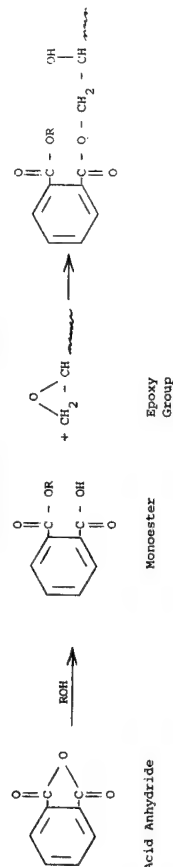


FIGURE 3

Amine Type Reactions



Acid Anhydride Type Reaction



Novolac Type Reaction



FIGURE 2 Different Copolymers formed by use of different hardeners

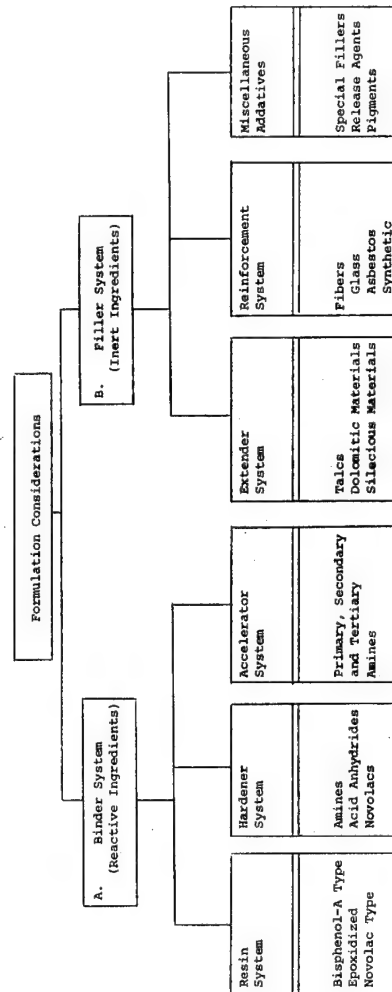


FIGURE 4 An outline of the variables which are included in epoxy molding compound formulating

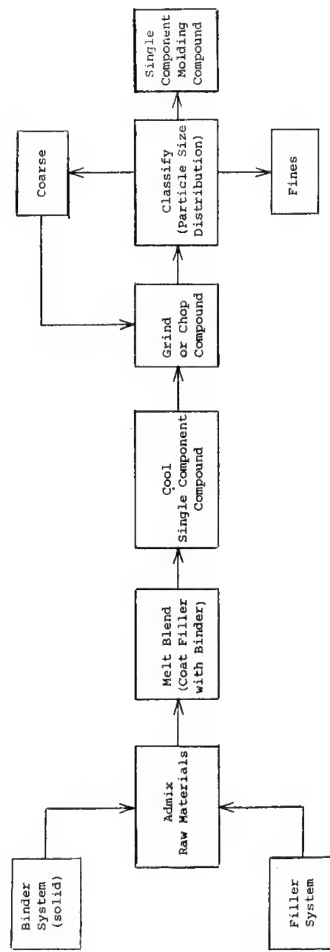


FIGURE 5 Melt blend fabrication method

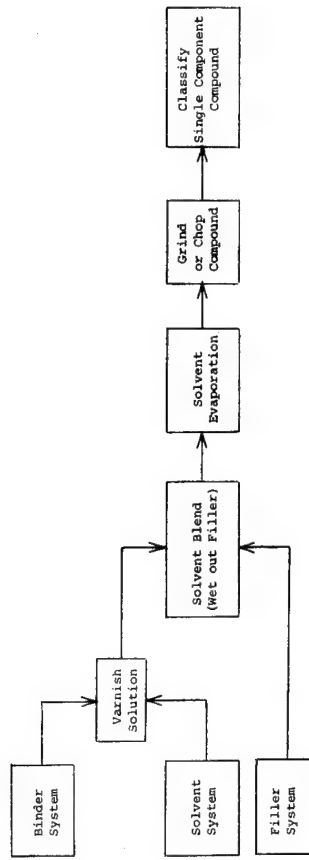


FIGURE 7 Solvent Blend Fabrication Method
(Used for Premix and Prepreg Type Compounds)

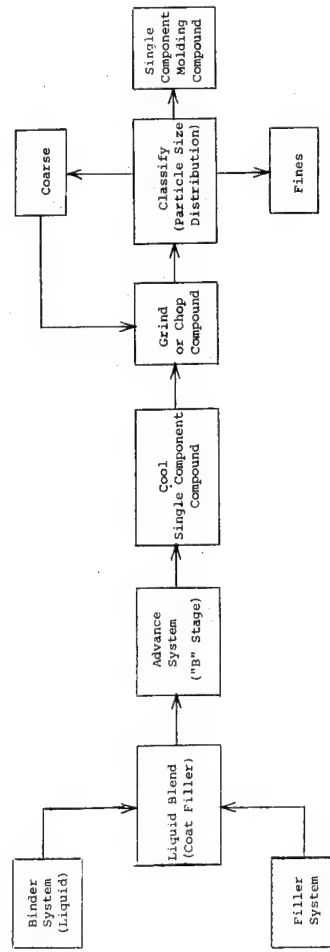


FIGURE 6 Liquid Blend fabrication method

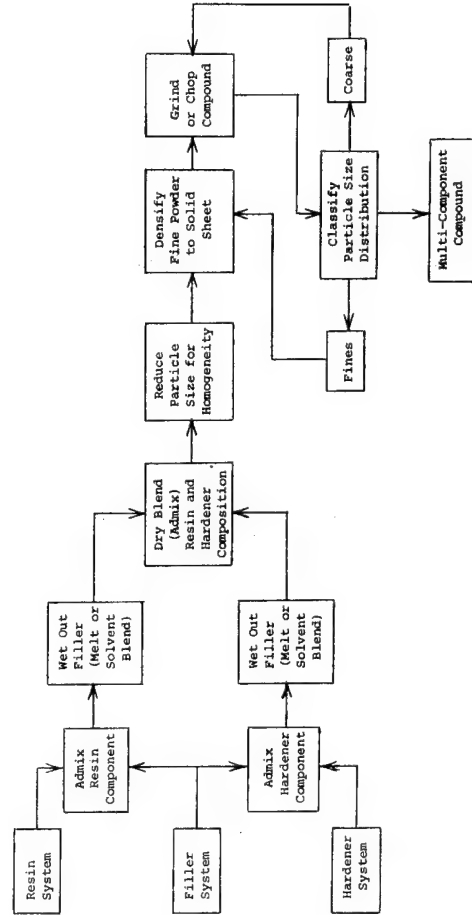


FIGURE 8 Dry Blend Fabrication Method

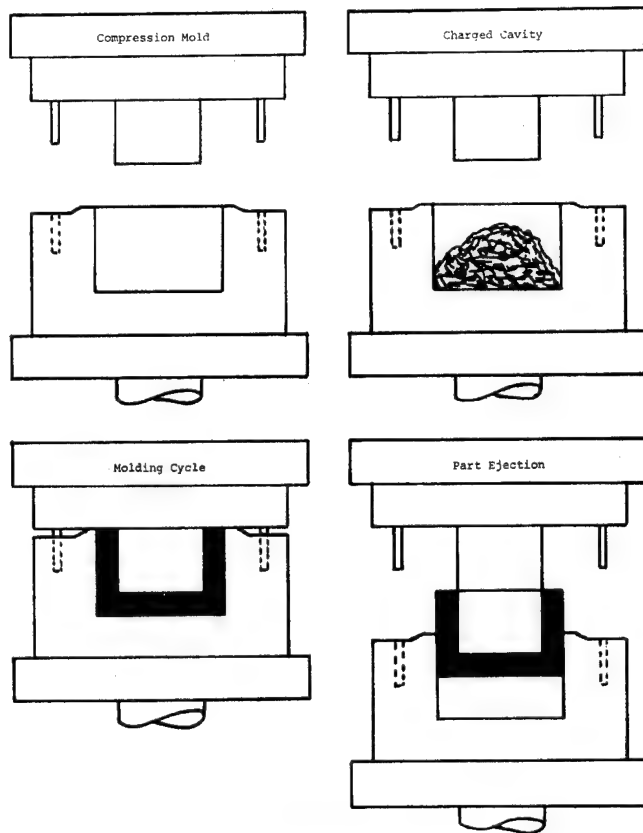


FIGURE 9 Compression molding cycle

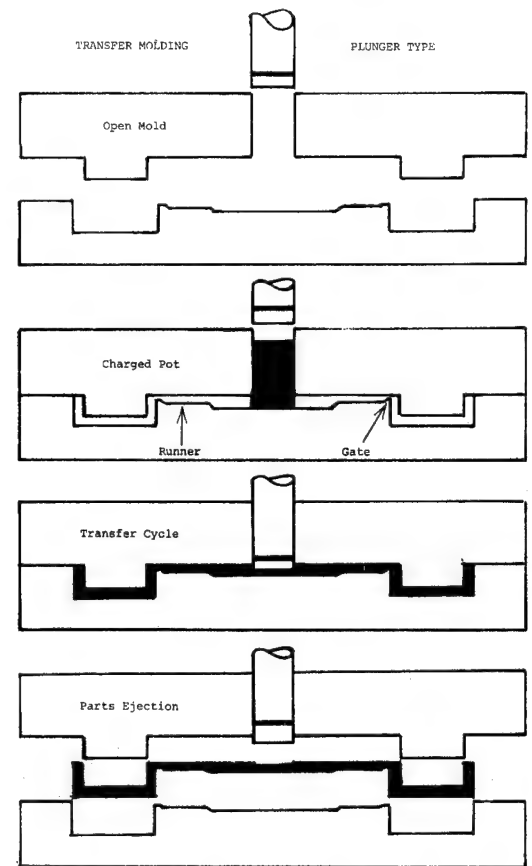


FIGURE 10 Transfer molding – Plunger type

TYPICAL PROPERTIES¹

(Compilation of Manufacturers' Published Data)

	Type I	Type II	Type III
Molding Parameter	High Flow/ Low Pressure Transfer	Low Flow/ Low Pressure Compression	Compression
Storage Capability	6 months @ 32°F to 1 yr. @ 72°F		
² Bulk Factor	1.5 to 2.5	1.5 to 5.0	3.0 to 15.0
² Specific Gravity	1.5 to 2.5	1.5 to 2.5	1.5 to 2.5
² Tensile Strength, psi, x 10 ³	5 to 10	7.5 to 15	15 to 30
² Flexural Strength, psi, x 10 ³	10 to 16	15 to 25	25 to 60
² Compression Strength, psi, x 10 ³	---	25 to 35	30 to 40
² Impact Strength			
Izod Notched ft. lbs./in.	0.3 to 0.5	0.5 to 10	10 to 50
Water Absorption 24 hrs. @ 77°F, %	0.05 to 0.10	0.05 to 0.10	0.05 to 0.10
@ 122°F, %	0.35 to 0.50	0.10 to 0.40	0.10 to 0.30
Coefficient of Thermal Expansion in./in./°C (-30°C to + 30°C) x 10 ⁻⁶	2.0 to 5.0	1.5 to 4.0	1.5 to 2.5
Coefficient of Thermal Conductivity cal/sec/cm ² /°C/cm, x 10 ⁻⁴	6 to 16	12 to 35	12 to 18
Deflection Temperature, °F	300 to 550	350 to 550	300 to 600
Mold Shrinkage, in./in., x 10 ⁻³	2 to 20	1 to 20	1 to 10

¹ According to ASTM Test Methods

² Assumed tests were run at room temperature (77°F)

FIGURE 11 Typical properties¹

02

TRANSFER MOLDING OF ELECTRICAL COMPONENTS

W. D. Norring

and

John Delmonte

Furane Plastics, Inc.

Los Angeles, California

The introduction of transfer moldable epoxies to electrical industries several years ago has brought a tremendous surge of interest to these compounds. Ease of flow at comparatively low pressure and low temperature has kindled interest in the prospects of improved insulation for the electrical industry. The beneficial effects of pressure applied, 100 per cent solids, insulation, are summarized in Figure 1.

The insulation engineer will recognize the significances attached to the claims which are tabulated in Figure 1. They are so germane to a discussion of transfer molding that an eclectic review will assist an analysis.

PRESSURE

One may reason that the greater the pressure the more complete the penetration. There are limits. Excessive pressures may mechanically disturb elements which are being protected by the applied insulation. As suggested by elements contained in the X-ray of Figure 2, there are fine connections, capacitors, and semi-conductive devices which high molding pressures would disarrange. Moderate pressures which, for the time being, we will describe as 1000 psi or under, are desired, and fulfilled by transfer molded epoxies. Many successful commercial wire wound units, such as solenoids and small transformers, are insulated in this manner. See Figure 3 illustrating transfer molded units of the Square D Company. The interrelations of pressure/time/temperature are examined in greater detail later in this paper.

PENETRATION

The optimum penetration of 100 per cent solids forming dielectric as an insulation in an electrical component, is accompanied by elimination of voids whether due to gases, shrinkage, or dead air spaces. When a solid insulation media replaces voids, there is an improvement in heat transfer; a reduction of corona losses; less chance for moisture vapor penetration; and attenuation of noise levels due to vibration. Pressure applied insulation (via transfer molding) accomplishes these objectives much more expeditiously than manually applied or

gravity poured insulation.

GAS ENTRAPMENT

Gases may well be one of the contributors to voids noted in the paragraph above. For reasons already cited, pressure application will keep this to a minimum. It should also be noted that the inherent low cure shrinkage of the epoxies, the inertness of the transfer molded epoxy insulation relative to other materials, concomitant with electrical components; and its volatile-free cure mechanism, qualify them as negligible contributors to formation of gaseous by-products.

CONSOLIDATION

Pressure application of insulation about diverse components is, in effect, a process of consolidation or integration. The insulation is the matrix or continuum in which are imbedded copper, steel, silicon, ceramics, phenolics, glass, etc. - all elements or compounds comprising the component. This matrix must have the mechanical soundness and dielectrical qualities essential to performance reliability. Properties of transfer molded EPOCAST 400 epoxies are illustrated in Figure 4 to indicate these characteristics which go hand-in-hand with good moldability.

SAVINGS

The accomplishment of the objectives noted in the paragraphs above is especially succinct when it is noted that there are important savings in manufacturing costs. The current trend towards transfer molded epoxies by major electrical and electronic manufacturers is a measure of the acceptance of this concept.

PRESSURE/TIME/TEMPERATURE

Fundamentals of transfer molding epoxies are closely related to the behavior of materials under pressure, time and temperature variables. This sequence of processing operations is noted in Figure 5.

As suggested in Figure 5, the behavior patterns of the transfer molded epoxies are very much controlled by the applied pressure, temperature and elapsed time. To study these fundamental variables an experimental molding press, manufactured by Furane, equipped with a sensor to measure ram movement, see Figure 6, has allowed us to record characteristics of commercial molding materials. These data have been important as quality control measures on manufactured molding materials of the EPOCAST 400 series. A group of charts are reproduced covering the following conditions, involving flow into an EMMI spiral flow mold (see Figure 7).

Of course, the spiral flow mold behavior is not necessarily a guarantee of performance for an infinite variety of mold configurations, though it does provide a reference base as a standard - the flow distance and the time duration of flow at different pressures and temperatures provide molders with basic information that is needed.

Much more can be said and will be published upon these new techniques of pressure applied insulation. We hope that the elucidation of fundamental processing variables and examination of the characteristics of transfer molded

epoxies have demonstrated their latent potential.

Editor's Note: Figures 2, 3, 4 and 6 referred to in this paper, were not available at the time of publication.

ACKNOWLEDGMENT

Credit is given to Square D Co. for the use of the illustration on their transfer molded units.

Credit is given to John Currie of Furane's laboratories for developing the flow property charts.

PRESSURE APPLIED INSULATION

WILL

1. Achieve maximum penetration into voids,
2. Minimize entrapment of gases,
3. Consolidate diverse elements into a unified package, and
4. Effect savings in manufacturing costs.

FIGURE 1

GRANULES OF TRANSFER MOLDED EPOXIES (T.M.E.) ARE:

1. Measured and placed in transfer pot, or
2. Preformed and placed in transfer pot, or
3. Preformed, preheated, and placed in transfer pot.

PRESSURES ARE APPLIED BY HYDRAULICALLY ACTUATED RAM, T.M.E. FLOWS UNDER PRESSURE THROUGH:

- a. Sprue to
- b. Runners to
- c. Gates into
- d. Mold cavities.

T.M.E. encapsulates the components and cures, under pressure, into an infusible and insoluble state.

FIGURE 5

- A. EPOCAST 403-S3 - molded at 250°F., and 300°F., under pressures of 250, 500 and 100 psi.
- B. EPOCAST 414 - molded at 300°F., and 350°F., under pressures of 500 and 100 psi.
- C. EPOCAST 409 - molded at 250°F., and 300°F., under pressures of 250, 500 and 1000 psi.

FIGURE 7

ENCAPSULATION OF ELECTRICAL COMPONENTS UTILIZING
LIQUID RESIN MOLDING TECHNIQUES

Robert F. Zecher

Hull Corp.

Hatboro, Pa.

and

Frank Bell

Hysol Corp.

Olean, N. Y.

INTRODUCTION

There have been essentially two processes used for the encapsulation of electrical and electronic components in various thermosetting plastics resins. The first utilizes one of several methods for coating the devices with various polymers in essentially liquid forms. These processes may be characterized by casting the resin into a form or mold around the device, or coating the device by spraying or dipping it. The other technique for encapsulation uses the process known as transfer molding to actually mold the device in a coating of plastics which starts as a dry powder, is liquefied under heat and pressure, and then finally cures into its final hardened state.

Recently, a new process has emerged which combines some of the features of liquid resin techniques with the higher productivity of transfer molding. Essentially, various resins in liquid form, can be injected under pressure into a multi-cavity mold held under pressure by a clamping device such as a hydraulic press. Initial investigations of this process indicate some success in eliminating some of the shortcomings of both liquid resin processes and transfer molding. Although liquid resin molding will probably not replace either liquid encapsulation or transfer molding entirely, it will help to bridge a gap between the two processes in two ways. First, apparently a wider range of materials and, hence, material properties may be possible with liquid resin molding than with transfer molding, thereby enabling the encapsulation of devices which, so far, have required end properties unobtainable by transfer encapsulation; and second, liquid resin molding takes place at lower pressures, making feasible the encapsulation of more fragile devices, and also lowering equipment and tooling costs significantly.

LIQUID RESIN MOLDING - A SIMPLE PROCESS

Basically, what we call liquid resin molding consists of injecting a premixed resin such as epoxy, polyester, or silicone into a mold which may be single or multi-cavity and which is clamped together under pressure. Depending upon the particular formulation of material used and essentially the pot life of the mixed resin, the storage reservoir may either consist of a tank of premixed resin and hardener together with associated fillers, catalysts, etc., or a metering, mixing and dispensing machine may be substituted for the storage reservoir to provide essentially instantaneous blending of resin and hardeners for prompt injection into the mold. Schematic diagrams of these two systems are shown in Figures 1 and 2. From either the storage reservoir or the dispensing machine, the material is fed into a metering and injection chamber which may be single or multiple, depending upon the particular equipment involved. This chamber may be cooled, left at ambient temperature, or heated, depending upon the particular resin system used.

The clamping device for holding the two mold halves together could be quite simple in the case of a single cavity development mold, but for greater production rates and efficiencies, it should be an automatic machine built along the lines of a compression molding press. The mold is either placed between heated platens of the press, if it is a hand mold, or if a production mold, is bolted into the press frame permanently and contains its own heat, ejection system, insulation, and so forth. Devices can be transported in and out of the mold with loading fixtures similar to those used in transfer molding or loaded directly as in the case of hand molds. The press then clamps on the devices under pressure and holds until the injection cycle begins.

The beginning of the injection cycle, which is usually semiautomatic and again analogous to transfer molding, starts with actuation of the cylinder for injecting the metered charge of resin through a nozzle system into the parting line of the mold. From the side of the mold the material flows through a runner system and then through gates into the cavities. Simultaneously with injection, the cure timer is started and times the cure or polymerization portion of the cycle. The injection nozzle may be retracted at any predetermined time during the cure cycle when the material has set sufficiently in the runner so as not to back out of the mold. One important feature of the injection nozzle may be a cooling water jacket which prevents the nozzle from overheating and precuring any material not used in the previous shot. The system should be designed so that essentially all material metered into the injection cylinder is used for one shot and a completely fresh batch of material enters for the next cycle.

At the conclusion of the cure cycle, the main press opens exposing the molded parts or freeing the hand mold for removal. At the same time the reservoir system transfers a fresh batch of material into the injection cylinder for the next cycle. In essence, then, liquid resin injection is very similar to transfer molding and, in fact, is slightly more automated since material feeding is a part of the cycle and not manual. A simple injection system tied into an existing transfer press is shown in Figure 3.

FEATURES OF LIQUID RESIN MOLDING EQUIPMENT

There are several key factors in liquid resin molding which point to specific equipment design features. First, it can be assumed that liquid resin molding takes place at essentially lower pressures than transfer molding. Much of the prototype work done so far indicates pressures as low as 15 psi and more generally

in the range of 35 to 50 psi are more than adequate to fill large production molds. Because of this factor, clamping pressure per square inch of molded part area can be considerably lower than in transfer molding. Reducing clamping pressure by one-half for a comparable molded part area greatly reduces the cost of the equipment and still leaves plenty of safety margin. Conversely, for the same clamping tonnage as in a transfer press, the platen area might be enlarged to approximately twice its previous size with corresponding increase in total molded part area.

Except for this reduction in clamping tonnage necessary, the other main features of a transfer press system are desirable. These include a fast approach of the clamping ram until within approximately one-half inch of closing and then a closely controlled closing speed to both protect the mold from damage and also to allow the inserts to be properly seated into lead slots, etc. Hydraulic systems afford much better control of the press movement and instantaneous response to surges in injection pressure, and, of course, whatever system is used, the controls must be essentially automatic once the cycle is initiated by push buttons.

The injection system itself may consist of several interchangeable components, depending upon the type of resin used, the size of the shot, and the best processing parameters for a particular job. If a storage reservoir is used for premixed material, it may be unheated or jacketed for either heating or cooling depending on the pot life and attendant storage problems. A metering, mixing and dispensing machine may also be heated or unheated, depending upon the particular material, and while it affords the user freedom from concern about pot life problems, it also represents some inflexibility in changeover to different materials or varying ratios of resin and hardener for different specific end purposes. In either case, those familiar with transfer molding techniques will have to become familiar with the problems of liquid resin handling which are essentially cleanup problems.

From either the storage reservoir or the dispensing machine, the material is fed to the injection cylinder system. Here again, a hydraulic actuating system provides more positive control over speed and pressure than an air system and may be taken right off of the main press hydraulic supply. In many cases it may be desirable to convert a transfer press for liquid resin molding, and in this case, hydraulic pressure from the old transfer system may be used to actuate the injection system very nicely.

The chamber where the resin is actually metered must have an adjustable stop and must be at least roughly sized for the general shot range desired on the particular machine. As previously mentioned, it is essential that all resin be injected from the cylinder during any one cycle, thereby minimizing the possibility of precured resin setting up in the injection system. For practical purposes, it is impossible to construct an injection system which will accurately dispense from a few grams to several hundred grams, so interchangeable injection cylinder sizes may be desirable. The actual volume of the shot is regulated by adjusting the stroke of the cylinder.

A jacket on the injection cylinder allows the material to be brought up in temperature or held back, depending again on the behavior of the particular resin system. Raising temperature may reduce viscosity of the material, but of course, also shortens this pot life. Cooling the nozzle may be the best answer to eliminating hangup in that area as the problem of heat transfer from the mold into the nozzle must be considered. Disassembly of the entire injection cylinder and nozzle system must be fast and simple in the case of inadvertent setup of the material. Sophisticated equipment should include a method for purging the entire system with a solvent, particularly in the case of shorter pot life materials.

CONVERSION OF OLDER TRANSFER PRESSES

The injection system is so similar to the transfer process that it would seem very feasible to convert older transfer into liquid resin molding machines. In fact, there seems to be no reason why the injection system can't be added as an option to the older press so that both the injection system and the transfer molding capabilities are left intact. Since the injection system can be automatic, whereas the transfer actuation is generally semi-automatic, a slight change in the control function may be needed, but most of the other features of a good transfer system can be utilized, such as the speed control, pressure adjustments, timed cure cycle, automatic retraction, and so forth.

New equipment may be considered in light of either (1) versatility for both transfer molding and liquid injection molding, or (2) economy, in which case liquid injection molding will be the less expensive of the two. Because of the expected reduction in required clamping pressure explained above, the liquid injection press, for the same molded part area, will require a smaller clamping system. By the same token, the injection system will require considerably less pressure and volume of oil than the transfer system. This arrangement may be particularly desirable where a prototype machine is needed for experimental work or for encapsulating very small parts.

MOLD DESIGN

At the present time, it appears as though hardened tool steel molds are still necessary for encapsulation of components with projecting leads or terminals. While the use of considerably lower injection pressures in the case of the liquid resins has been noted, there is still the problem of damage to the mold surface by misplaced leads or terminals being clamped under full tonnage. The additional cost of hardened steel molds over softer steel is not that much greater considering the possibility of damage to a softer mold under continuous production use.

Mold surfaces must still be highly polished and chrome plated for easy removal of the material. The same care is necessary in designing the V-slots and guides for lead wires, and, of course, the same close tolerances must be held on the individual cavities to produce uniform parts. Ejection systems will still be necessary in the case of many parts, particularly where epoxy is used, and all of the other features of transfer molding, such as vacuum molding, pin positioning systems, and so forth, may or may not contribute to the flexibility of the liquid resin molding process.

In the case of hand molds, however, it may be possible to construct much simpler and less expensive experimental and prototype tooling. Here softer steels, or perhaps aluminum, may definitely be used, and there is much experimental work going on with the use of epoxy tooling. In this respect, liquid resin molding may make one of its most significant contributions in reducing the cost of research and development.

In the actual layout of the mold runner and gating system, there will be several differences from transfer molds. First, as already mentioned, injection will be on the parting line, thereby eliminating the transfer pot and plunger. Runner systems can apparently be considerably smaller than with molding compounds because of the reduced viscosity of the material. Gates may also be reduced, in proportion to the amount and the size of filler particles in the material, particularly fibrous type fillers. Venting appears to be about the same as with

molding compounds. Lead slot tolerances must be closely held, again as with transfer molds. However, there appears to be a definite reduction in the amount of flash obtained with liquid resin molding, primarily due to the accurate control of injection pressures as well as to the very low range of these pressures.

MATERIAL CHARACTERISTICS

From the material supplier's viewpoint "injection molding" with liquid epoxy and other thermosetting materials is a natural development which evolved from a need to do a good job better. As indicated previously, liquid resin molding will help bridge the gap between transfer molding with powders and encapsulation by casting or potting with liquids. The process will not necessarily replace these established techniques, but it will provide another tool for solving some production problems. The process of molding with liquid resins is really quite simple, but what about the materials themselves? I will limit my remarks to what should be expected of liquid epoxy materials suitable for molding by injection.

Actually, there is nothing surprisingly new about the materials used in this process. They are still compounded from resins, hardeners, fillers, pigments and catalysts which the formulator must concoct into a usable material with a balance of characteristics required by the user. It is a fact that many of the standard liquid epoxy materials now available can be made to work in equipment such as described previously.

If I may presume to roughly structure the component encapsulation problem, I would consider the following among the main factors:

1. The encapsulant must provide the device with sufficient insulation and protection from hostile environments. Certainly, this is what we are trying to accomplish.
2. The encapsulant must be applied without damage to the part.
3. The overall encapsulation process must be a reliable and economical means of producing such parts.

With regard to the first factor, insulation and protection, the widespread acceptance and use of liquid epoxy materials testifies to their suitability for casting and potting a variety of electrical and electronic devices. Table I lists most of the more important electrical and physical properties of cured liquid epoxies. These values are typical and, in some cases, may be improved by formulation changes. It appears that the freedom to formulate for specific end properties is greater with liquid epoxies than with powders. However, such changes can only be made to the extent that they do not unduly upset the balance of properties. Some of the basic trade-offs are listed in Table II.

The second factor, not damaging the part, brings up the most important advantages of a liquid epoxy molding system compared to transfer molding. Liquid materials can now be molded at temperatures as low as 200°F., and probably lower in the future, and at pressures down to 5 psi.

The third general area of importance in the encapsulation process, reliability and economy of the system, necessarily involves the interrelationship of the equipment and material. The handling characteristics of liquid epoxies are quite important in determining whether or not the liquid molding process lends

itself to a particular production situation. A range of characteristics of epoxy liquids can be expected. For example, mixing ratios can be expected to vary with particular resin/hardener systems, but can be made ranging from 10:1 to 2:1 for convenience in hand or automatic mixing.

Viscosity of mixed and unmixed components at room temperature will cover a wide range from less than 100,000 up to 750,000 centipoise, depending upon end properties required. Heating of the components before mixing may facilitate de-airing and mixing. Warming the mixed material may be possible to facilitate feeding by the equipment. As the material is injected into the heated mold, it quickly reaches a very low viscosity which requires little injection pressure.

Filler content can be up to 70 per cent with higher percentage possible if warming can be used to help reduce the viscosity. Fillers are the same as those widely used in liquid epoxies for casting and potting. A possible advantage of liquid epoxies over molding powders is the ability to incorporate some types of fillers which are not commonly used in transfer molding powders.

Workable pot life of these liquid epoxies is highly dependent upon the molding cycle time required. If hand mixing is used, pot life of eight hours or more may be desired at some sacrifice of increased molding cycle time. If rapid cycle times of say 30 seconds at 300°F are desired, it would be advisable to use a mixing/metering/dispensing machine to feed the injection cylinder. This briefly explains the reason behind the two feed systems which were shown schematically.

Gel time on a 300°F hot plate can be faster than 15 seconds although this seems to be a practical working limit.

Molding cycles of 30 seconds at 300°F have been obtained with some liquid epoxies in ten cavity hand molds. Since a finite time is required to inject the material and fill the cavities, cycle times are somewhat dependent upon equipment and mold design.

Post cure of around 150°C for 16 to 24 hours is recommended for parts molded in liquid epoxies, to assure attainment of desired end properties.

Clean up of the feed mechanism and tubing may be accomplished by flushing with solvents such as MEK or toluene.

Price of liquid epoxies suitable for pressure molding should not vary greatly from the epoxy molding powders in use today. Depending upon the desired end properties, different raw materials must be used and will determine price. However, the very important overall economies, i.e., total cost of one system versus another, have not been determined.

In summary, liquid epoxy resin molding can be made to work for the encapsulation of electrical and electronic devices. There is nothing surprisingly new about the materials and their cured properties, although certain handling characteristics have been modified to permit their use in more automated production equipment. Liquid epoxy resin molding will find a place among transfer molding and casting and potting techniques as a tool to be considered in solving encapsulation production problems.

TABLE I

TYPICAL PROPERTIES OF CURED LIQUID EPOXY SYSTEMS

ELECTRICAL (@ 1kHz where applicable and 73°F)

Dielectric Constant	3.5 to 5.0
Dissipation Factor	0.01 to 1.001
Dielectric Strength	500 volts/mil
Volume Resistivity	5×10^{15} ohm-cm
Surface Resistivity	5×10^{15} ohm

PHYSICAL (after appropriate post cure)

Tensile Strength	8,000 to 12,000 psi
Compressive Strength	25,000 to 30,000 psi
Coefficient of Thermal Expansion	30×10^{-6} in/in/°C (30-90°C)
Heat Deflection Temp.	up to 175°C
Thermal Conductivity	$10 \text{ to } 13 \times 10^{-4}$ cal/sec/cm ² /°C/cm
Linear Molded Shrinkage	0.5 to 1.0%
Operating Class (IEEE)	up to H

TABLE II

May Require Some Compromise in These Properties
(NE - No Noticeable Effect)

Optimizing This Property

	<u>Electrical</u>	<u>Physical</u>	<u>Handling</u>
Minimum Molded Shrinkage	(NE)	Lower Flexural Strength	Higher Viscosity
Longer Flow	(NE)	(NE)	Longer Cure Cycle
Low Molding Temperature	(NE)	Increased Coeff. of Thermal Expansion	Longer Cure Cycle Reduced Pot Life
Short Mold Cycle	General Decrease	Brittleness	Reduced Pot Life
Thermal Shock	(NE)	Lower Heat Deflection Temp.	Reduced Hot Strength
Increased Heat Deflection Temp.	(NE)	Lower Flexural Strength (Brittleness)	(NE)
Improved High Temp. Electrical Properties	(NE)	Lower Flexural Strength (Brittleness)	(NE)
Reduced Coefficient of Thermal	(NE)	Lower Flexural Strength (Brittleness)	Shorter, Stiffer Flow
Increased Thermal Conductivity	(NE)	Lower Flexural Strength (Brittleness)	Shorter, Stiffer Flow
"Flameout"	Slight Decrease	(NE)	Increased Viscosity
Reduced Post Cure	General Decrease	General Decrease	Shorter Pot Life
Lower Viscosity	(NE)	Lower Thermal Conductivity	Voids Due to Turbulence
Reduce Flash	(NE)	(NE)	Higher Viscosity

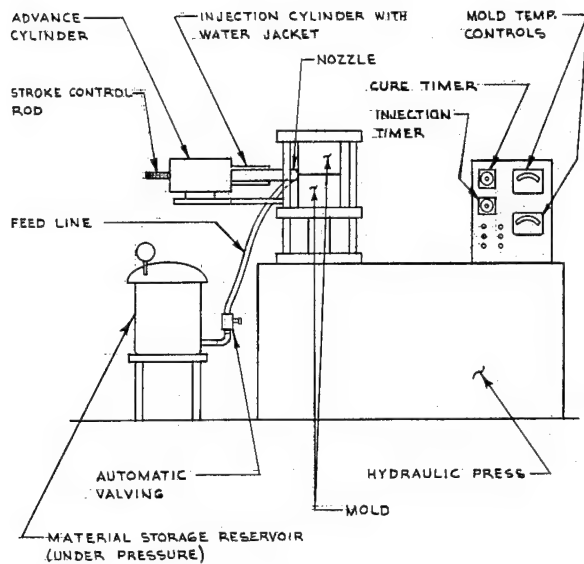


FIGURE 1 Liquid resin molding equipment with storage reservoir for pre-mixed resin system

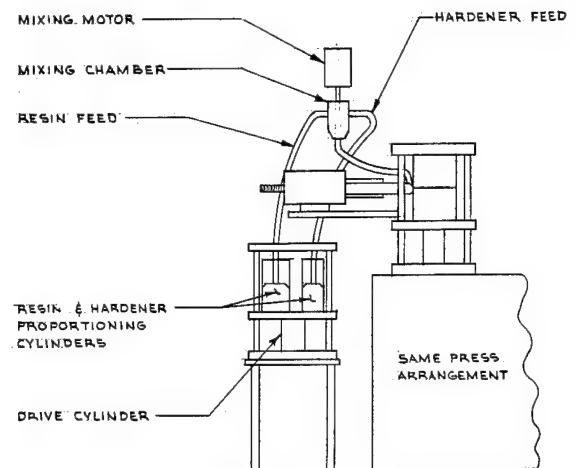


FIGURE 2 Same equipment with metering, mixing, dispensing unit in place of storage reservoir

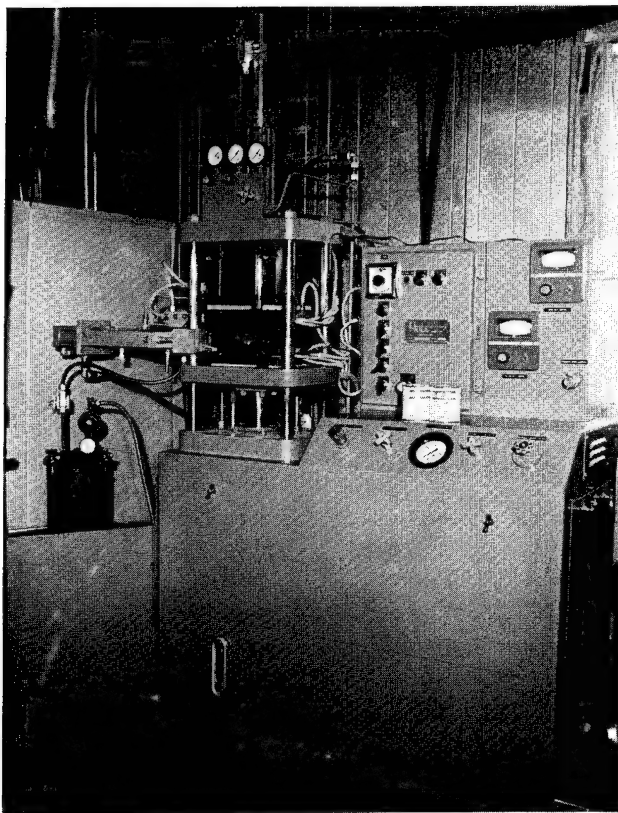


FIGURE 3 Small transfer press equipped with liquid resin injection system to inject on parting line of hand mold.

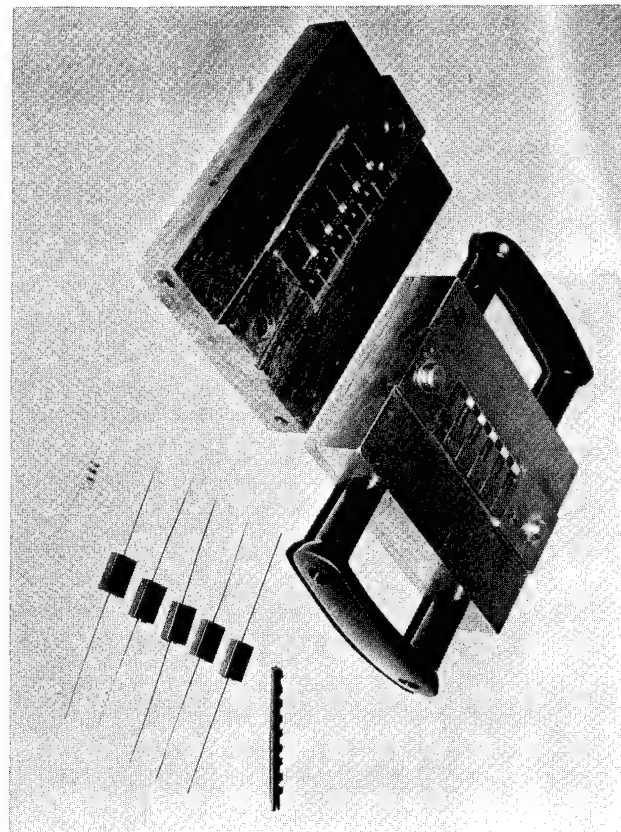


FIGURE 4 Mylar capacitors encapsulated in epoxy by liquid resin molding. Note modification to transfer mold runner to extend to edge of mold for parting line injection.

VAPORIZATION OF ORGANIC PLASTICIZERS*

Leo A. Wall, Joseph H. Flynn

and

Sidney Straus

Polymer Chemistry Section

National Bureau of Standards

Washington, D. C.

ABSTRACT

The kinetics of the molecular vaporization process of 21 plasticizers were investigated in detail. By both isothermal and nonisothermal kinetic methods, it was evident that 11 were quite pure single compounds while 10 were clearly mixtures of compounds. For the single component species internal energies for vaporization and rates of volatilization are listed. The internal energies of vaporization are about one-half or less of values one can estimate from the additive factor method of Small. Thus, solubility parameters based on our experimental values are low by about 30 per cent. From this and previous work on n linear alkanes, it is concluded that in the molecular vaporization process, the large organic molecules studied evaporate approximately as spheres and hence low values for the energy of vaporization are obtained. Consequently, the difference between our experimental energy and that estimated from solubility parameters is the energy for extending the molecule in a vacuum environment.

INTRODUCTION

Recent developments in thermogravimetric theory¹ and the availability of instrumentation suggested that the study of the kinetics of the molecular vaporization process for many relatively large organic compounds could be rapidly explored. Our interest grew out of our investigations of polymer decomposition.^{2,3} In order to theoretically interpret the experimental measurements of the thermal volatilization (decomposition) of polymers, it is essential to have knowledge of the critical size for vaporization, i.e., the molecular weight at which a given polymeric structure must decompose in order to evaporate. Vaporization energetics are also related theoretically to solubility, structural and cohesive energy density phenomena.⁴ Preliminary to this work an extensive study⁵ was made of the vaporization of four linear alkanes, C₁₉, C₂₄, C₃₆ and C₉₄.

*Based on research supported by the Advanced Research Project Agency, Washington, D.C. 20301

EXPERIMENTAL

A thermogravimetric instrument capable of determining rates of volatilization or evaporation under both isothermal and nonisothermal conditions was used. The apparatus consists of an electrobalance capable of accurately measuring weight with a precision of a tenth of a milligram with 1-20 mg samples (our standard sample weight was 10 mg), an electronic recorder and a pyrometric controller cam driven for nonisothermal experiments or a stepless controller capable of maintaining a constant temperature up to 600°C with an accuracy of $\pm 0.5^\circ\text{C}$. The sample and weighing mechanism was in a vacuum system which was pumped on by a high-capacity oil diffusion pump and mechanical fore pump. The pressure was monitored with a Pirani gauge. During the runs the pressure rarely exceeded 10 microns. The critical component in the apparatus is a cylindrical furnace eight inches by two inches inside the vacuum system. The sample, 10 mg, is suspended in the center of the furnace in a cylindrical region one inch by one inch diameter where the temperature has been mapped and found to be constant within 1°C . A monitoring thermocouple is also positioned in this region. For every plasticizer listed in Tables I and II a nonisothermal run was carried out. This data is presented in Figure 1. Then for each substance a series of isothermal rates were determined at various temperatures chosen on the basis of the nonisothermal data, see Figure 1.

The dimensions of the vessel in which the sample is suspended and sample size will cause some variation in the observed rate of volatilization. A simple molecular vaporization process from a constant surface area should have a "zero" order weight loss,¹ i.e., $\frac{dc}{dt}$ equals a constant, which we found when a pure compound was measured. Our maximum variation in rate was a factor of two with a twenty-fold variation in sample size, or two-fold variation in the height of vessel or the cross-sectional area of the vessel. Simple molecular vaporization of pure compounds gave in our experience very good horizontal isothermal $\frac{dc}{dt}$ versus C, where C is the fraction of the initial sample weight volatilized. Our experimental rates were of the order of 10^{-2} min^{-1} in all the figures shown. Since the sample size was constant at 10 mg and the vessel diameter four mm, the rates were of the order of $1.3 \times 10^{-5} \text{ g cm}^{-2} \text{ sec}^{-1}$.

RESULTS

In Figure 1 we present the fraction of the various plasticizers volatilized as the temperature is increased at the rate of $1.5^\circ\text{C}/\text{min}$. Comparison of the results suggests that the plasticizers listed in Table I and designated by capital letters are showing "zero" order weight loss kinetics and hence are essentially single or pure compounds. Notice that the curves for these compounds are as a class more vertical and very similar to each other. On the other hand, compounds listed in Table II and designated by lower case letters are spread over a larger temperature range. These are evidently mixtures of oligomers as one expects from the nature of their manufacture.

All the lower case designated plasticizers, Table II gave isothermal rates of vaporization results similar to the one shown in Figure 2. The downward curving lines depict the rate behavior at the three temperatures 287, 297 and 303°C . These curves were graphically obtained from the chart recording the weight of sample as a function of time. There is no simple way to determine a single activation energy for such a composite process using the Arrhenius method, since we know that both order and activation energy are varying with conversion. However, a procedural method is available from thermogravimetry theory. For nonisothermal runs

such as are shown in Figure 1, it follows,¹ provided the conversion and temperature are independent variables, that

$$\log F(C) \cong \log \frac{AE}{R} - 2.315 - 0.457 \frac{E}{RT_{\text{non}}}$$

where $F(C)$ is the integrated function of conversion. For isothermal runs

$$\log F(C) = \log A + \log t - \frac{E}{2.3 RT_{\text{iso}}}$$

where t = time and T_{iso} is a constant. Thus, at the same conversion on both the isothermal and nonisothermal weight loss curves, we can equate the two expressions to obtain

$$(\log t)_{\text{iso}} = b - 0.457 \frac{E}{R} \left(\frac{1}{T} \right)_{\text{non}}$$

where b is a constant. At iso conversional points we can then plot log time of the isothermal run versus $\left(\frac{1}{T}\right)$ of the nonisothermal run and obtain a straight line relation, and an activation energy.

The more nearly the data yields a straight line the more closely a single activation energy describes the process.

In this manner an apparent activation energy was obtained for all the substances listed in Table II.

In Figures 3, 4 and 5 we show vaporization rate data for several plasticizers of increasing molecular weight and hence increasing activation energies. All three of these show isothermal rate versus conversion plots with horizontal sections.

Such "zero" order weight loss indicates that a quite pure single component material is vaporizing and the rate values of the horizontal sections are plotted according to the Arrhenius method. In each figure the data are also plotted according to the technique described above. It is seen that very good agreement is obtained.

In Tables I and II we have tabulated all the data obtained on the "pure" and "impure" plasticizers, respectively.

Column one lists the letter symbol for the particular substance; column two, its name; column three; its empirical formula; column four, its sp. gr., at the temperature listed in column 5, and column six, their molecular weights. The other columns of data will be subsequently discussed more thoroughly below.

DISCUSSION

Following kinetic theory we assume that the rate of molecular vaporization in moles per sec at temperature, T , is given by

$$\frac{dn}{dt} = \frac{\alpha p_v A}{(2\pi MRT)^{1/2}} \quad (1)$$

where α , the accommodation coefficient is assumed to be one, A the area, M the molecular weight; R the gas constant, p_v the equilibrium vapor pressure. Since p_v is the equilibrium constant for the liquid-vapor process under study, we may write

$$\frac{dn}{dt} = \frac{1.01 \times 10^6 \alpha A}{e(2\pi MRT)^{1/2}} \times e^{\frac{\Delta S_v}{R}} e^{-\frac{\Delta E_v}{RT}} \quad (2)$$

The experimental activation energy determined in the usual fashion is then nearly identical with the internal energy change, ΔE_v , of the vaporization process. From the above equation it is seen that the Arrhenius slope relates to ΔE_v by

$$\frac{d \ln \frac{dn}{dt}}{d(1/T)} = \frac{T}{2} - \frac{\Delta E_v}{R} \quad (3)$$

For a vaporization process it follows that

$$\Delta E_v = - \frac{R d \ln \frac{dn}{dt}}{d(1/T)} + \frac{RT}{2} \quad (4)$$

In Tables I and II we list values of ΔE_v obtained by adding $RT/2$ to the usual Arrhenius activation energy.

Addition of another RT quantity gives the value for the enthalpy, ΔH_v , since

$$\Delta H_v = - \frac{R d \ln \frac{dn}{dt}}{d(1/T)} + \frac{3}{2} RT \quad (5)$$

These thermodynamic quantities are subject to some change with temperature. However, since specific heat data for these plasticizers are not available, they were not corrected to a standard temperature. Thus, in Table I we list in column seven the ΔE_v values obtained at the temperature listed in column eight. In Table II we list such results under the heading " ΔE_v ", the apparent internal energy, since the materials studied were mixtures.

The internal energy for vaporization, at least for small molecules is related to the solubility parameter, δ , by

$$\delta = \left(\frac{E_v}{V} \right)^{1/2}$$

where V is the molar volume. The ratio of $\Delta E_v/V$ is termed the cohesive energy density. From the above relation it is of interest to estimate solubility parameters using our experimental energies of vaporization and compare them with solubility parameters calculated by the method of Small.⁴ This method assumes additivity of the quantities $(\Delta E_v V)^{1/2}$ and devises a table of additive factors, F , for various organic groupings such that

$$\sum F = (\Delta E_v V)^{1/2} \text{ and } \delta = \frac{\sum F}{V}$$

We used these factors and relations to calculate ΔE_v for comparison with our experimental quantities. In Table I we list these quantities in column nine.

Comparison of these estimates with our measurements shows the former to be greater by about a factor of two or more. It is our conclusion that large flexible molecules vaporize in a highly compact coiled form and probably remain in a nearly spherical condition in the vapor phase. Consequently, for such molecules the solubility parameter, δ , is not given by the square root of the ratio $\Delta E_v/V$. The difference between the experimental and calculated energies shown in Table I is then evidently the energy for extending the molecules in the medium of a vacuum. In the last column of Table I we list the rate in $\text{g cm}^{-2} \text{ sec}^{-1}$ at the temperature shown in column eight. Thus one can estimate from the listed data the rate of vaporization at other temperatures in polymer mixtures if one assumes Raoult's law.

REFERENCES

1. Flynn, J. H. and Wall, L.A., J. Research NBS 70A, 487 (1966).
2. Wall, L.A., "Pyrolysis", Chap. V in Analytical Chemistry of Polymers, Part ii, Ed. G.M. Kline (Interscience, 1962).
3. Wall, L.A. and Flynn, J.H., Rubber Chem. and Tech. (5) 35, 1157 (1962).
4. Small, P.A., J. Applied Chem. 3, 71 (1953).
5. Wall, L.A., Flynn, J. H. and Straus, S., unpublished.
6. Modern Plastics Encyclopedia, Sept. 1962.

TABLE I

VAPORIZATION ENERGIES KCAL/MOLE OF "PURE" ORGANIC PLASTICIZERS

Key	Plasticizer	Formula	Sp.Gr. at	(6) °C	MW	Exper. ΔE_v , kcal mole	Temp., °C	Calc. ΔE_v (4)	Sol Para- meter, δ This work	(4)	Rate of Vap g cm ⁻² sec ⁻¹ x 10 ⁴ at T
A	0,0,0-tributylphosphorothioate	C ₁₂ H ₂₇ O ₃ PS	0.933	25	283	11	70	25	6.03	9.08	4.3
B	triethyleneglycoldi-pelargonate	C ₂₄ H ₄₆ O ₆	0.964	20	431	21	90	33	6.86	8.60	5.0
C	diisooctylsebacate	C ₂₆ H ₅₀ O ₄	0.916	20	425	13	91	35	5.29	8.70	7.3
D	2,2'-(2-ethylhexamido-di-ethyl-di-2-ethylhexoate)	C ₂₈ H ₅₃ NO ₅	0.956	20	484	19	103	40	6.12	8.89	8.5
E	didecylphthalate	C ₂₈ H ₄₆ O ₄	0.964	25	446	20	106	36	6.57	8.82	9.6
F	diisodecyl-4,5-epoxy-tetrahydrophthalate	C ₂₈ H ₅₀ O ₅	0.987	20	466	18	108	33	6.17	8.24	8.5
G	acetyltri(2-ethylhexyl)-citrate	C ₃₂ H ₅₈ O	0.983	25	570	16	115	47	5.25	9.05	9.1
H	ditridecylphthalate	C ₃₄ H ₆₆ O ₄	0.950	25	538	20	122	43	5.94	8.71	6.5
I	trioctyltrimellitate	C ₃₀ H ₅₇ O ₆	0.987	25	546	29	132	50	7.24	9.51	4.8
J	glyceryltriacetoxystearate	C ₆₃ H ₁₁₆ O ₁₂	0.955	25	1066	41	225	82	6.06	8.58	6.6
K	glyceryltrizcetylricinoleate	C ₆₃ H ₁₁₀ O ₁₂	0.965	25	1060	49	256	82	6.68	8.64	7.7

TABLE II

APPARENT VAPORIZATION ENERGIES FOR MULTICOMPONENT ORGANIC PLASTICIZERS

Key	Plasticizer	Formula	Sp.Gr. at 25 C	MW	" ΔE_v " kcal mole	at T°C
a	n-butylacetylricinoleate	$C_{24}H_{44}O_4$	0.928	397	30	92
b	polyethylene glycol (200)	$C_{12}H_{10}O_3(C_2H_4O)_x$	1.158	400	25	112
c	polyethylene glycol (400)	$H_2O(C_2H_4O)_x$	1.128	400	38	120
d	diethylene glycol distearate	$C_{40}H_{78}O_5$	0.96	693	25	148
e	polypropylene glycol (775)	$H_2O(C_3H_6O)_x$	1.004	775	40	165
f	polyethylene glycol (400) distearate	$(C_{17}H_{35}COOC_2H_4)_2O$	0.97	639	45	233
g	polyethylene glycol (600) dibenzozate	$(C_{14}H_{10}O_3$	1.141	800	51	235
h	polypropylene glycol (1200)	$H_2O(C_3H_6O)_x$	1.003	1200	48	244
i	polypropylene glycol (2000)	$H_2O(C_3H_6O)_x$	1.000	2000	50	290
j	polyethylene glycol (1000)	$H_2O(C_2H_4O)_x$	1.085	1000	53	297

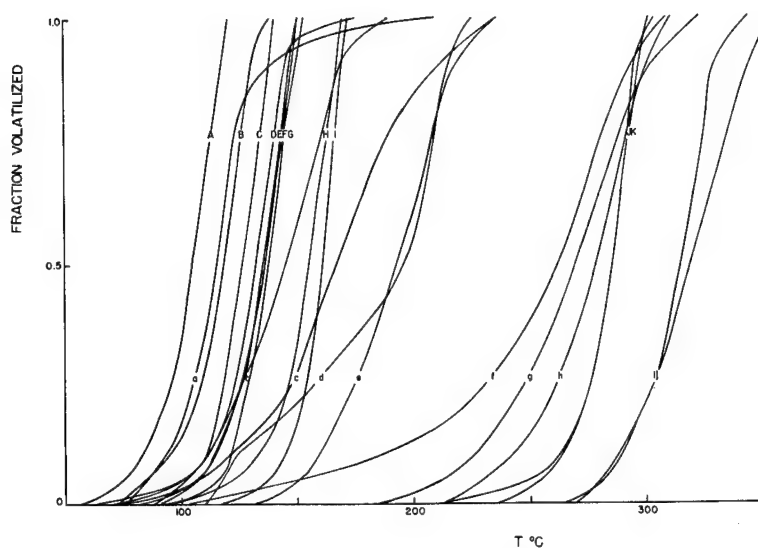


FIGURE 1 Thermogravimetry of organic plasticizers. Fraction volatilized as a function of temperature 15°C/min, see Table I and II for the names of the compounds.

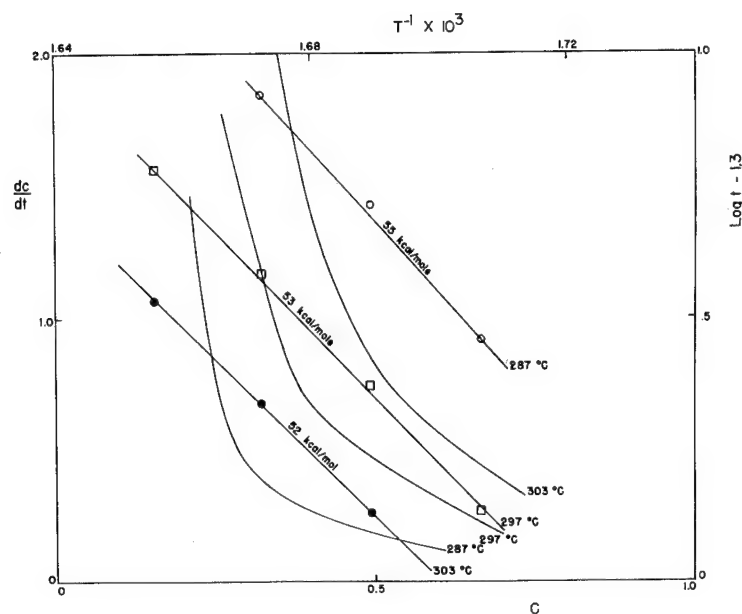


FIGURE 2 Vaporization of polyethylene glycol plasticizer. Sample size 10 mg, curve lines rate $\frac{dC}{dt}$ vs. fraction vaporized C. Straight lines plots of $\log t$ (isothermal) vs. $1/T$ (nonisothermal) used to determine activation energy.

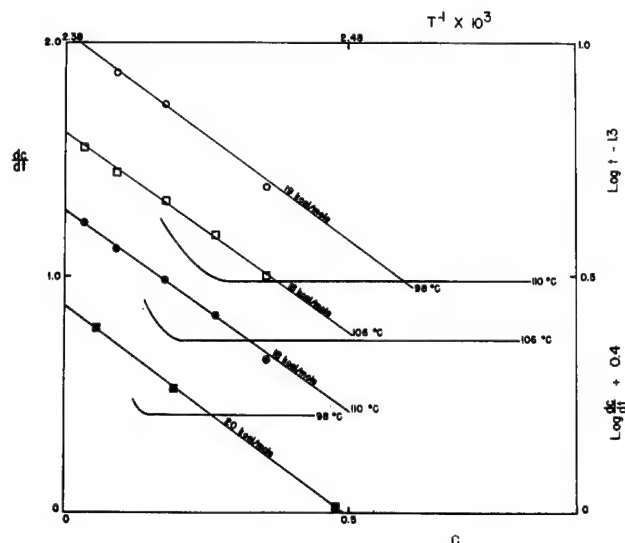


FIGURE 3 Vaporization of didecylphthalate (MW 446). Sample size 10 mg. Curves with horizontal section, rate, $\frac{dC}{dt}$, vs. fraction converted, C. Other lines activation energy determination, upper three lines $\log t$ (isothermal) vs. $1/T$ (nonisothermal), lowest line Arrhenius plot $\log \frac{dC}{dt}$ vs. $1/T$.

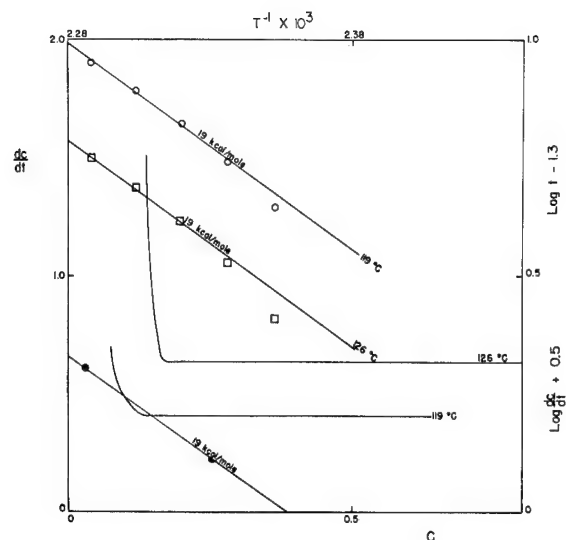


FIGURE 4 Vaporization of ditridecylphthalate (MW 538). Sample size 10 mg. Curves with horizontal section, rate, $\frac{dC}{dt}$, vs. fraction converted, C. Other lines activation energy determination, upper two lines $\log t$ (isothermal) vs. $1/T$ (nonisothermal), lowest line Arrhenius plot, $\log \frac{dC}{dt}$ vs. $1/T$.

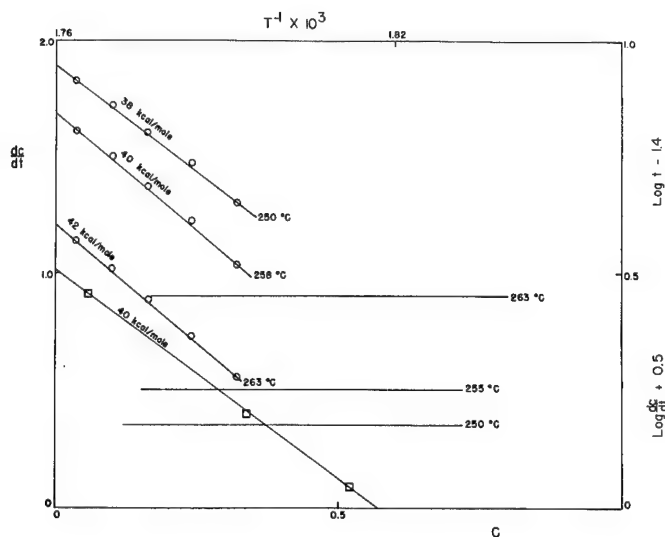


FIGURE 5 Vaporization of glyceryltriacetoxystearate (MW 1066). Sample size 10 mg. Horizontal lines, rate, $\frac{dC}{dt}$, vs. fraction converted, C. Other lines activation energy determination, upper three lines $\log t$ (isothermal) vs. $1/T$ (nonisothermal), lowest line Arrhenius plot $\log \frac{dC}{dt}$ vs. q/T .

PLASTICS IN ELECTRONIC INTEGRATED CIRCUITS

William MacCrehan

Materials Evaluation Div.

Westinghouse Corp.

Elk Ridge, Md.

The key element in an integrated circuit is the die on which the metallization patterns have been placed constituting the electrical circuit. The second element is the interconnection between the external leads and the internal bonding pad locations. For final assembly, a package to contain the die and to provide external leads for connection to the printed circuit board, is the conventional approach.

Advancements in the use of "plastics" has made the use of a glass/metal package or a ceramic package unnecessary in certain applications. With a major cost reduction between the use of conventional integrated circuit packages and plastics encapsulation of a "die frame" providing an integral assembly, the advantages of a plastics encapsulated integrated circuit assembly is well worthy of consideration in selected applications.

For commercial usage where a ready maintainability or end item low cost is paramount, plastics encapsulated integrated circuits have been successfully used by the millions. For military usage where severe environmental exposure or no system maintainability is possible, industry is still questioning the reliability of plastics encapsulated circuits.

The positive aspect of a plastics package are: accurate molded dimensions for automation of assembly, rugged construction for stock handling, and a relatively shock-proof assembly since all parts such as die, bond wires and internal/external leads are "locked in place".

The major area of concern is the ability of plastics encapsulated packaged circuits to stand up to environments in which changing temperatures under the presence of moisture are encountered. These environments are readily encountered in military applications and in space applications.

Because of the large reduction in package costs and the adaptability that molded plastics packages offer for mass production, the search for techniques for both manufacturing and testing to assure military level plastics packages is being aggressively pursued.

Testing activities for proofing of plastics encapsulated integrated circuits is being carried on by all major integrated circuit suppliers. Rome Air Development Center is conducting a major program in the testing of plastics encapsulated integrated circuits. Suggested tests in a proposed voluntary test program developed by RADC is shown in Figure 1.

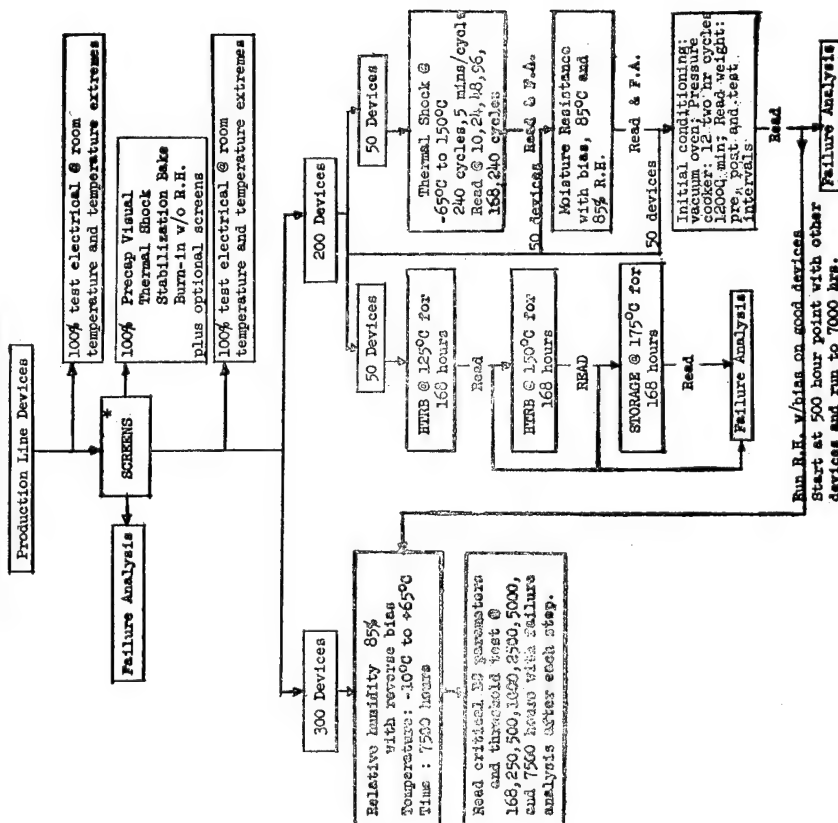
At the Westinghouse plant in Elkridge, Maryland, the focus has been toward providing a seal around the die and then encapsulating this "Hermetic" chip in the plastics outercoating. This process is known as GOLDILOX. Three areas are treated by an engineering approach to remove the cause of potential failures:

1. Protection of the interconnection patterns by a "glass overcoat".
2. Protection of bond junctions by a unimetal construction, viz, gold/gold, or aluminum/aluminum.
3. Protection of metallization process by a passivation process utilizing silicon nitride. Figure 2 shows the GOLDILOX construction. Tests for GOLDILOX are conducted under four major areas of stress:
 - a. Boiling water immersion - 72 hrs.
 - b. Pressure cooker - 48 hrs.
 - c. 85° temperature/ 85% RH/ 8 volts reverse bias - 1000 hrs.
 - d. Power burn in 125°C at 10 volts reverse bias - 2000 hrs.

SUMMARY

◀The merits of a low-cost plastics encapsulated integrated circuit that can meet both commercial and military applications provides a stimulus and a challenge that is rapidly being met by the integrated circuit industry. Constant engineering improvements coupled with selective stress testing to prove the reliability of plastics encapsulated integrated circuits is providing a product that is available in limited quantities. ▶As the advancement of technology to control the variables of the manufacturing process occurs, mass production availability of reliable plastics encapsulated integrated circuits will be a fact, not just fancy.

PROPOSED TEST PROGRAM



*All screens and tests will be run in accordance with the methods described in MIL STD 883
F.A. = Failure Analysis

FIGURE 1

GOLDILOX

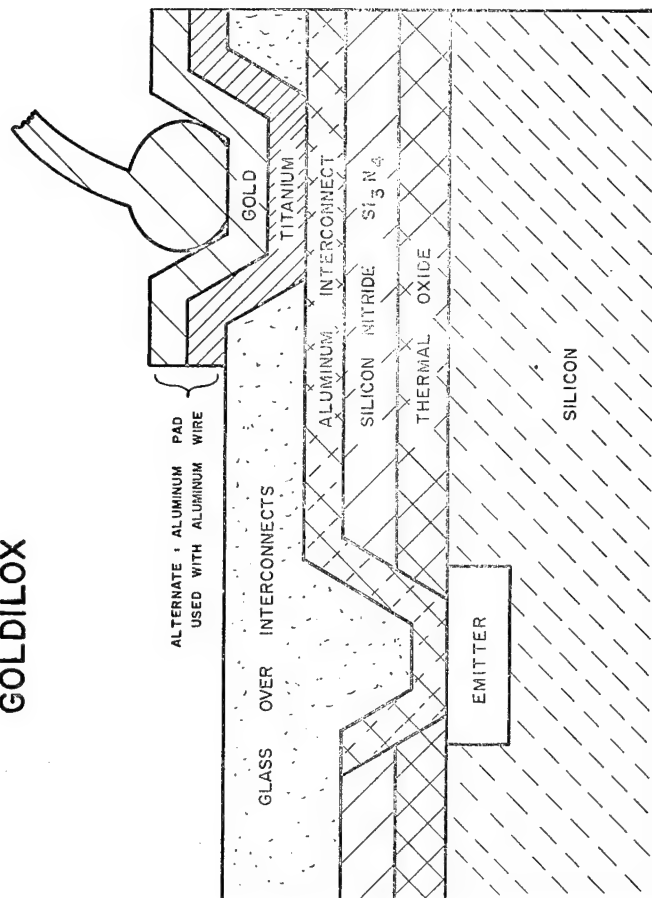


FIGURE 2

CIRCUIT DEPOSITION BY ENERGY BEAM IRRADIATION OF CERTAIN
METAL-CONTAINING HEAT SENSITIVE POLYMER COATINGS

T. F. Saunders, Dr. R. E. Dreikorn

and

Dr. M. F. Levy

Components Div.

International Business Machines Corp.

Endicott, N. Y.

The copper conductor lines shown in Figure 1 on the dielectric substrate were written by an argon laser. The blue material between the lines is a polymeric copper chelate that was decomposed by the laser to form the copper lines. The dielectric substrate is Nomex,¹ a fully aromatic polyamide.

The argon laser beam that wrote these lines is five mil in diameter and power levels comprising a few to several hundred milliwatts were used.

< This presentation is a report of a study performed at the Manufacturing Research Laboratory in the IBM Corporation, Endicott, New York, to develop an additive process for printed circuit technology. Electron and laser beams were used in this study. >

Figure 2 is a schematic copper formate-polyethyleneimine and is representative of the metal chelate polymers that were decomposed by irradiation with either electron or laser beams. These polymeric chelates are water-soluble containing in excess of 20 per cent solids as copper. To make conductor lines, these moderately viscous aqueous solutions were applied to the substrates by dipping and then air drying. After irradiation, the undecomposed chelate, between the lines, was removed by washing with water for reuse.

< The application of energetic beams to decompose an organic material is not new. However, the use of a low-cost, water-soluble chelate with a high concentration of metal, that is nonvolatile and easily applied in any thickness through spraying or dipping, represents a new process for the manufacture of printed conductor lines. >

Figure 3 illustrates a palladium spiral conductor produced by irradiating a palladium polyethyleneimine chelate with the electron beam. Figure 4 shows why spiral patterns are useful. The energy input varies with exposure velocity; therefore, from the center of one spiral to the edge, the exposure can vary approximately 300 per cent. An optical and electrical inspection of the entire spiral permits selection of the best section of the spiral. The energy density of the

¹Registered trademark of the E.I. duPont Co.,
Wilmington, Del.

section is then calculated. Confirmation of the energy density given by these calculations is accomplished by a linear traversing mechanism that makes straight lines three inches long as seen in Figure 1. These are convenient to measure.

The range of electron beam energy densities that were used in this study extended from two to approximately 100 joules/cm². By varying the accelerating voltage, electron beam current, and revolutions per minute of the sample, any density range required could be obtained. From the results of this wide variation in power input, the following generalizations could be made pertaining to the influence of electron-gun parameters on the conductivity of the printed conductor formed in the exposed chelate. These generalizations are in diagram form in Figure 5.

The resistance of a printed conductor line formed on irradiation of a polymeric chelate with an electron beam is plotted against energy density. The idealized result would be "U" shaped as illustrated in the slide. This shape means that conversion from high-resistance chelate to low-resistance conductors occurs only after a critical energy density is applied to the chelate. The curve further shows that low resistance conductors can be obtained through a wide range of energy densities and that after an excessive energy density has been exceeded, all the copper is evaporated and a high-resistance residue remains.

However, the experimental data forms a parabolic curve and shows that the conductor becomes increasingly resistive and critical (a narrower range of energy density for approximately the same resistance) with the accelerating potential (E_{BB}). Increased accelerating voltage leads to deeper penetration or more material to convert per unit charge. At increased energy densities and decreased voltages, the beam penetrates the coating by stages performing greater conversion; this is manifest by decreased resistance.

Similarly, an increase in the time that a beam dwells at a given location causes an increase in the conversion to copper and a decrease of the resistance. This explains the effect of residence time (T_R) on the resistance. Finally, with an increased current, the increased flux of electrons blunts the parabola because the I^2R effect increases the conversion to copper and thereby lowers the resistance.

The choice of inorganic salt to formulate the polymeric chelate is based on the desired metal conductor and the vigor of the decomposition reaction when irradiated. Some systems such as copper nitrate-polyethyleneimine produced poor printed conductor lines at all tested energy densities; however, other systems produced consistently fair-to-good lines. The exothermic character of the nitrate system led to ejection of copper metal from the line during the decomposition. A Thermal Gravimetric Analysis (TGA) survey was made of many possible systems as an aid in selection of the chelate that would produce better conductors.

Figure 6 shows the TGA traces of copper nitrate and copper formate polyethyleneimine chelates as well as polyethyleneimine itself. The TGA is a plot of weight of remaining sample against temperature as the sample is heated. These TGAs were accomplished in vacuum with a heating rate of 25°C per minute. The slope of the weight-loss curve indicates the vigor of the decomposition. These curves show that the poor printed conductors that resulted with the nitrate are due to the explosive nature of the decomposition. The formate trace is typical of a very mild evolution of gaseous products and almost parallels the endothermic decomposition of the polyethyleneimine.

The residue after TGA decomposition of the formate chelate agrees with the theoretical amount of copper plus a small quantity of char resulting from the organic portion of the chelate. The small residue in the nitrate chelate supports the

conclusion that the copper was ejected from the substrate. The TGA survey permitted an evaluation of the degree of dependency of the decomposition rate with power input. The copper formate polyethyleneimine chelate was the most controllable system evaluated.

After considerable electron beam work was done, an argon laser was made available and used because of its convenience and because it represented only thermal energy. Working in vacuum systems requires pumpdown time and the installation of machinery and apparatus in constrained volumes. The use of a laser eliminated the rapid expansion of the hot gaseous decomposition products with vacuum that can be destructive to the conductor. Further, the laser is electrically neutral. So, an electrical charge is not accumulated on the dielectric substrate to cause unknown side effects. Lastly, in working with the electron beam, the electrons are easily stopped, so the coating thickness is more critical for electron reduction.

Calculations based upon exposure velocity spirals made in copper formate-polyethyleneimine with an argon laser beam, five mil in diameter, indicated good printed conductor lines at energy densities of approximately 100 joules/cm²; so straight printed conductor lines were produced at various energy densities as indicated in Figure 1. Figure 7 illustrates a photomicrograph of one line. The dark streak on the top of the line is a condensed reaction product that washed away in water during the development process.

The grainy texture of the line is readily apparent in Figure 7; the resistance values of the best lines obtained prior to development ranged from 20 to 30 ohms/in. The data indicated that approximately 100 joules/cm² produced printed conductor lines of highest conductivity and that the conductivity was dependent upon the energy input. The lines were approximately 15 mils wide and both the width and depth of conversion were reduced with reduced energy input.

Metallographic cross-sections were made of some printed conductors and the resistivity of the conductor was calculated to be approximately 600 times greater than bulk copper. This is indicative of the open grainy-structure in the metal. During the development in water, normally used to remove the unaffected chelate located between the printed conductor lines, the major portion of the copper was also removed because of poor adhesion to the substrate.

This poor adhesion of the decomposed copper to the substrate had been predicted. Two methods were tested in an effort to improve the adhesion. One method required incorporating a material in the substrate surface that reacted with the decomposed copper as illustrated in Figure 8. In this instance, a slurry of copper oxide powder and epoxy resin was coated on the substrate. The blue-colored-chelate was coated over this undercoating with the intention that the hot metal would form a bond with the imbedded oxide. Unfortunately, the resulting oxide-epoxy surface was rough, and the heat loosened the oxide particles. This caused open gaps in the copper printed conductor. The second method illustrated in Figure 9, was a pre-coating of the plastics substrate with a Neoprene or polysulfone that would lock copper to the substrate by adhesion.

Both of these methods were successful.

The lines that had greatest survival in the development process were those formed in the 100 joule/cm² range. Thus, a feasible method of promoting copper-line adhesion to the substrate was now at hand.

The high resistance of the printed conductors that survived development was the

next consideration.

Tests indicated that the printed conductor lines were brittle and it was difficult to make connections to them by soldering. These characteristics suggested impure copper or imperfect sintering. Printed conductor lines were examined with a Scanning Electron Microscope. This instrument with its large depth of field is able to show the character of the copper in the printed conductor that was produced by laser irradiation of the chelate.

Figures 10 through 12, inclusive, produced by a Scanning Electron Microscope, illustrate a copper conductor produced after an argon laser beam exposed copper formate polyethyleneimine. The magnifications are 200, 500 and 1000X. The blue chelate between the lines has been removed during the development process and the open porous structure of the metal is shown.

This type of structure can result from the evolution of the gaseous reaction products and the rapid solidification of the copper that occurs after the laser passes. These factors and the dissolved gases could produce a brittle, high-resistance conductor.

The printed conductor lines were electroplated to fill the voids and gaps and reduce the resistance. The resulting printed conductor lines were of good quality, but economically unsound. Electroless plating of printed lines made of palladium by the electron beam was successful too, but the cost of the palladium chelate limits its application. Finally, multiple sweeps of a laser beam on a copper conductor line were tested at various energy densities to obtain additional sintering and purification. The results of this can be summarized by stating that if the energy input is sufficient to remelt or resinter the metal, the substrate was burned and adhesion of the copper was lost. Also, the surface tension of the liquid metal caused it to form into a ball ahead of the beam and spill over the edges of the silt; if melting did not occur on the subsequent sweeps of the beam, the resistance and brittleness would be unchanged.

Finally, an economic analysis indicates that if greater energy densities were available with more powerful lasers than those in existence at this time, and the probable speed of printed conductor line writing were significantly increased, then reasonable conductors could be formed in copper polyethyleneimine chelates. However, the process would be more costly than the current subtractive process as used in the industry.

ACKNOWLEDGMENT

The authors are grateful to their colleagues in the Manufacturing Research Laboratory whose work has contributed to these results. Mr. O. Abolafia for the TGA analysis, Mr. E. C. Baldwin for the electron beam irradiation and analysis of results, and Mr. T. J. Stewart for photography, metalographic cross-sections and X-ray analysis, the late Mr. B. J. Serafin for conducting tests and offering suggestions, Mr. A. D. Tencza for laser exposures, and especially Dr. G. S. Kozak, Manager of Advanced Chemical Technology.

- 07

OXYGEN INDEX: KEY TO PRECISE FLAMMABILITY RATINGS

Kenneth B. Goldblum

Specialist, Product Technology

Polycarbonate Research & Development

General Electric Co.

Pittsfield, Mass.

There is a multiplicity of tests which have been developed and modified for rating the flammability of plastics. In most of these cases, a definite sample geometry is used. The sample is ignited in a very specific and arbitrary way. The description of the "end point" varies from test to test. To compound the difficulty of interpretation of the results, such terms as "non-burning", "self-extinguishing", "slow burning", "burning rate", have been used. A study of many of these methods recently completed, led to the conclusion that all flame tests were necessarily arbitrary from the points of view of (1) the manner in which the sample is ignited and (2) the definition of the end point.

A further drawback of a number of the flammability tests is that they are run under non-equilibrium conditions, that is, the end point of the test in time, which has been arbitrarily set as satisfactory, is far too short for the equilibrium to be achieved between the heat lost to the environment and the heat generated by the combustion of the material. Under such conditions, it is no wonder that the present flammability methods have been the despair of people seeking to develop and rate flame retardant materials because of the wide variability in the results.

Back several years ago, Drs. C. P. Fenimore and F. J. Martin of the General Electric Research and Development Center's Combustion Laboratory came up with a new way for evaluating the flammability of plastics. Their search was prompted by the need for greater knowledge of the physics and the chemistry involved in the burning of plastics.

< The Fenimore-Martin or Oxygen Index Test, the names by which it has come to be known, has been designed to overcome, as far as possible, the three drawbacks of ignition, end point, and operation under non-equilibrium conditions as well as the arbitrary nomenclature used in describing flame test results. > In this new procedure, known mixtures of oxygen and nitrogen are fed through a glass bead bed over the sample in the form of a stick about 1/4 in. wide by 1/8 in. thick by about 4 in. to 6 in. long. The sample stick is held vertically at its lower end in a clamp in the center of the glass chimney.

The sample is ignited at its upper end with a hydrogen flame. The manner of ignition is of great importance. Let us for a moment consider the principal on which this test is based. We are trying to determine the limiting per cent of

oxygen in the gas mixture fed which will just "sustain the candle-like burning of a stick of polymer", to quote from Fenimore and Martin's paper in Modern Plastics for November 1966. Obviously, it is necessary to achieve equilibrium between the heat removed by the gases flowing by the sample and the heat generated by the burning of the sample. To achieve this equilibrium, it is clear that the original ignition must be well done, that is, the sample must be very well ignited. Otherwise, the sample is not being given a fair chance to reach equilibrium when the per cent oxygen in the mixture is near the limiting, or critical value. Not enough heat will be coming from the combustion to overcome the deficit from under ignition. An over-ignited sample needs only time, usually about 30 to 60 seconds after ignition is complete, to come to equilibrium with the heat removed by the flow of gases past the sample. The thorough ignition of the sample, therefore, cannot be overemphasized if consistent and reproducible results are to be had.

As far as the end point is concerned, the test results are such that the Oxygen Index values obtained by any one of several end points are very close together, if not essentially the same, with only the stipulation that the sample is well ignited and has been allowed to burn at heat equilibrium for a long enough time. Thus, regardless, if the end point is measured by the sample burning steadily for three, four, five or even six minutes, or if a limit is taken, such that the sample burns three inches, the final results are very close to being the same. But we will examine the reproducibility of the results in greater detail later.

In addition to taking care of the problems of ignition, end point, and operation under equilibrium conditions, the reporting of the data is done in an unequivocal manner. The value of the Oxygen Index in numerical terms is reported rather than expressing the results in vague, qualitative words, the meaning of which even within the context of a particular test method is subject to debate. The Oxygen Index value is a precise, reproducible number which can be used to rate the flammability of plastics.

Considering the apparatus itself, Figure 1 shows a precommercial setup. The oxygen and nitrogen are fed through reducing valves to precision reducing valves by means of which the pressure can be controlled to closer than 0.1 psi. The gas in each case is metered by means of a calibrated orifice and led to the bottom of the bed of glass beads. The beads help to mix and disperse the gases evenly over the cross-section of the glass chimney. The sample is mounted and ignited with the hydrogen flame as described above.

Figure 2 shows a close-up view of a burning sample. Generally, the procedure used is to arbitrarily select an oxygen-nitrogen mixture and ignite a sample. If the sample burns for the preselected time or length, the oxygen content of the mixture is reduced, first in larger steps of about 2 per cent oxygen, until a ratio is reached at which the sample will not burn for the preselected time or length after proper ignition. The oxygen in the mixture is then increased by smaller stages to the point where the sample will just burn the standard criterion. This point is checked with three to five samples to make sure of its reproducibility. The percentage of oxygen in the total gas mixture reported to the third significant figure is the Oxygen Index for the material under test.

Nearly a year ago, in ASTM D20.00, Section 20.30.03, on flammability directed a Task Group to study this new method. The Task Group chairman, J. L. Isaacs, of the Major Appliance Laboratory, General Electric Company, Louisville, organized a "round robin" with twelve participating laboratories. These laboratories, some of which had homemade versions of the Fenimore-Martin equipment, were to test four materials and report their Oxygen Index values using their own interpretation and procedures of how the test should be made. The results of these tests are given in

Table I in coded form as far as the identity of the individual laboratories is concerned.

Aside from Labs 3 and possibly 11, which reported consistently high results, the results are in surprisingly fine agreement considering that no standard procedure was used. Some later work by Lab 3 indicated that flowmeter trouble and insufficient ignition might have been the causes for the differences found. In the case of Lab 11, it was felt that good ignition had not been carried out and, therefore, this point was stressed in an earlier portion of this paper. A statistical analysis of the data, omitting the data from Lab 3, led to the conclusion that "repeatability within a lab is less than between labs". This unusual statement can only mean that the differences found at their worst are very small.

Parenthetically, I would like to emphasize at this point that Underwriters' Laboratories is one of the participants in the ASTM "round robin" and that UL has joined in this work with great enthusiasm. Further, the excellent interlab agreement on the first "round robin" has been so encouraging that those of us on the Task Group feel confident that the Oxygen Index Test will set a new record in ASTM D-20 for the shortest period of time between the initiation of the Task Group and the acceptance of the method by the Society!

What can be done with the Oxygen Indices for various materials once we have them? The first thing that can be done is to line up materials on the basis of their Oxygen Index values. This is shown in Table II.

Then, as experience with this method is obtained, it will be possible to put opposite each material a list of successful applications in which the particular material has been accepted as satisfactory as far as the flammability characteristics are concerned. Eventually with such a list, one should be able to find either an exact application described or one that is a close match. The materials from the list that will meet the flammability requirements, then, will have the Oxygen Index opposite the application or a higher one, depending upon the other considerations involved in the material selection. If one were to put his mind to it, there might be enough data on hand already to make a good start on such a table.

To this point in the discussion, we have been discussing a more or less standard thickness sample, of say, 1/8 in. We feel intuitively that there must be some effect on the Oxygen Index from the thickness, because it certainly is much easier to get twigs burning than, say, a four-inch log! We have made such a study on polycarbonate sheet from a thickness of about 12 mils up to 250 mils. These findings are shown in Table III.

As expected, the thinner specimens burn more readily. Whether the variations from about 80 mils to 250 mils is real or due to experimental error is debatable at present. However, when the fact is considered that polycarbonate is a difficult material to burn because of its tendency to both char and drip, we might lay the differences at the door of experimental error is debatable at present. However, when the fact is considered that polycarbonate is a difficult material to burn because of its tendency to both char and drip, we might lay the differences at the door of experimental error. This conclusion is borne out to some extent by the wider scatter in the data of the ASTM "round robin" on the polycarbonate. However, experience has already shown that the higher the Oxygen Index for a material, the broader the scatter in the results. Regardless of the argument on this point, it is clear that below 80 mils, the Oxygen Index decreases as the sample thickness decreases.

To summarize, a new flammability method is available which eliminates most of the drawbacks of ignition, definition of end point effects, non-equilibrium operation, and fuzziness in the description of the results. <The method allows the precise rating of materials on a numerical basis and provides the opportunity to match up proved applications versus Oxygen Index values to enable the designer and user of plastics materials to select the right plastics in a more precise way, as far as flammability is concerned. >

TABLE I

ASTM D-20.30.03 "ROUND ROBIN" #1 OXYGEN INDEX TEST DATA

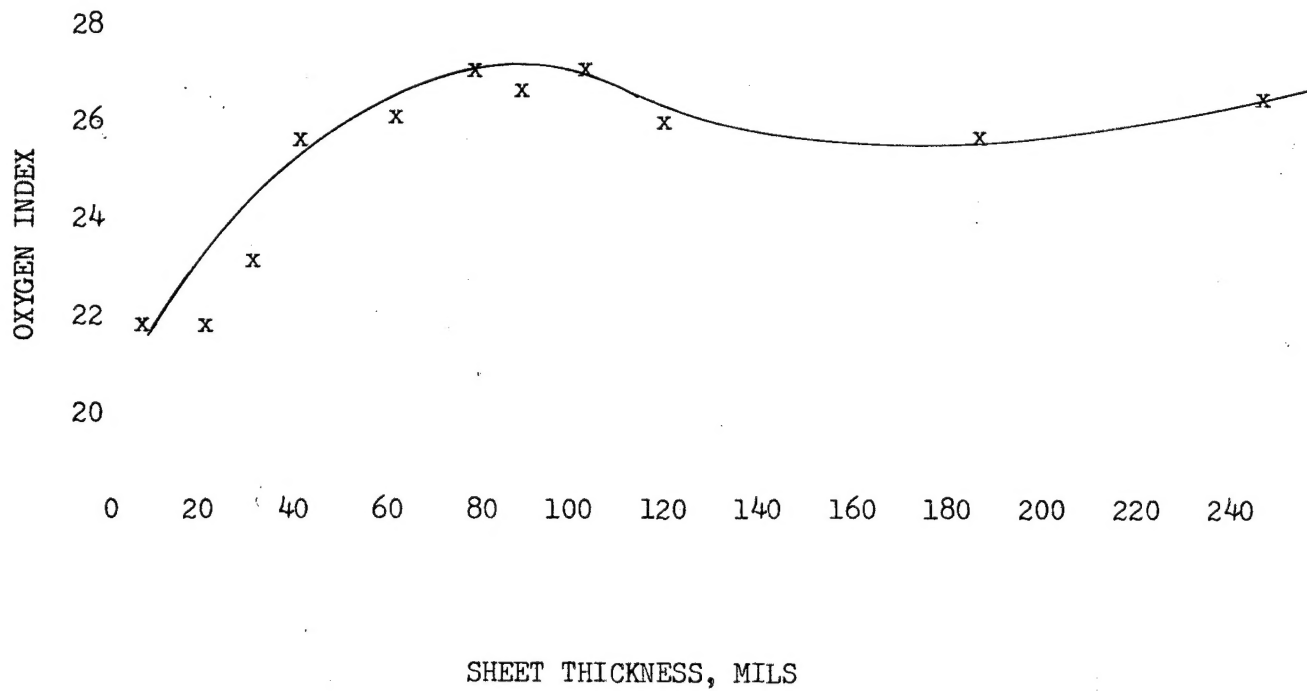
<u>LAB NO.</u>	<u>MATERIALS</u>			
	<u>PP</u>	<u>PMMA</u>	<u>PC</u>	<u>PVC</u>
1	17.6	17.7	25.0	40.0
2	17.8	17.8	23.7	37.6
3	19.8	19.7	25.9	41.8
4	17.5	17.5	23.9	39.6
5	17.4	17.5	25.3	42.0
6	17.5	17.7	24.4	40.3
7	17.7	18.1	24.9	41.3
8	17.5	17.7	24.4	41.8
9	17.2	--	25.2	--
10	17.5	17.5	22.9	36.6
11	18.3	18.5	26.5	41.5
12	17.6	17.5	24.9	41.2

TABLE II

OXYGEN INDEX RATING OF POLYMERIC MATERIALS

<u>MATERIAL</u>	<u>PER CENT OXYGEN</u>	<u>MATERIAL</u>	<u>PER CENT OXYGEN</u>
Acetal	16.2	Nylon 6-6	28.7
PMMA	17.3	Lexan ^(R) 3414-131 Resin	
PE	17.4	40% Glass	29.3
PP	17.4	Lexan ^(R) 3412-131 Resin	
SAN	18.1	20% Glass	29.8
PS	18.3	PPO ^(R) 534 Resin	30.0
ABS/PC Alloy	20.2	Polysulfone P1700	30.4
Noryl ^(R) 731 Resin	24.0	Lexan ^(R) 2014 Resin	31.5
Lexan ^(R) 101-111, -112 Resin	25.0	Lexan ^(R) DL444 (Experimental) Resin	39.7
Lexan ^(R) 141-111, -112 Resin	25.0	Lexan ^(R) DL444 Resin plus	
Lexan ^(R) Glass Resin	27.8	20% Glass	42.0
SE-1 Noryl ^(R) Resin	28.0	Polyvinylidene Fluoride	43.7
		Polyvinyl Chloride	47.0
		Polyvinylidene Chloride	60.0
		Polytetrafluorethylene	95.0

TABLE III



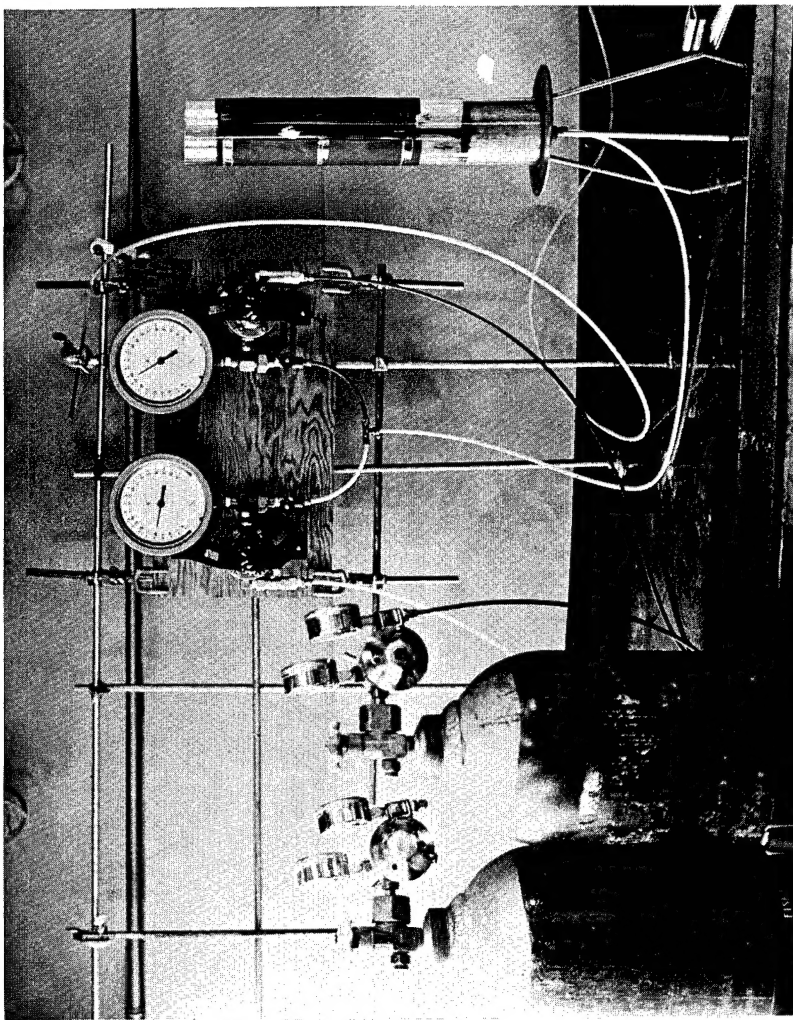


FIGURE 1 Oxygen Index Apparatus

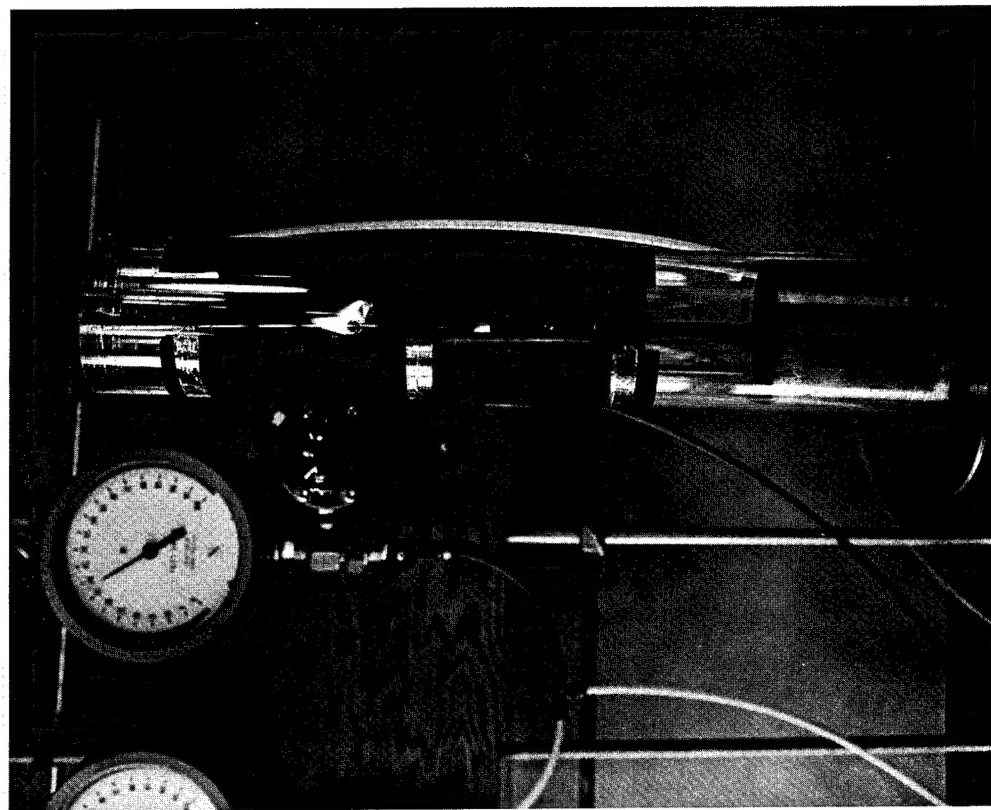


FIGURE 2 Closeup of burning sample

**INITIATION FEE
MUST BE ATTACHED
FOR PROCESSING.**



SOCIETY OF PLASTICS ENGINEERS, INC.

656 West Putnam Avenue
Greenwich, Connecticut 06830

MEMBERSHIP APPLICATION

PLEASE PRINT OR TYPE

Executive Office Use Only

I.D. No. _____

Ack. _____

Elected _____

I hereby make application for { ☐ admission into
☐ reclassification within
☐ reinstatement in } the Society of Plastics Engineers, Inc. in the grade of membership indicated below for which I believe I am qualified.
(See instructions or reverse side.)

Grade	Initiation Fees	Annual Dues	Foreign Dues	I wish to affiliate with the _____
<input type="checkbox"/> Senior Member	\$10.00	\$20.00	\$17.50	_____
<input type="checkbox"/> Member	10.00	20.00	17.50	_____
<input type="checkbox"/> Affiliate Member	10.00	20.00	17.50	_____ section.
<input type="checkbox"/> Student Member	None	5.00	5.00	(Geographical location. See listing on reverse side.)

Applicants Full Name _____

(First) (M.I.) (Last) (Citizen of) (Birthdate)

Please fill in both addresses and **CHECK THE ONE TO WHICH YOUR MAIL SHOULD BE ADDRESSED.**

☐ **BUSINESS:** Company Name and Division: _____

Position _____

Address _____ City _____ State _____ Zip Code _____

☐ HOME: Address _____ City _____ State _____ Zip Code _____

REFERENCES The By-Laws require the names of three references who are familiar with your work. One of them should be a member of the Society. Assistance in providing member-references, when needed, will be given on request.

1. _____ Address _____

2. _____ Address _____

3 _____ Address _____

STATEMENT OF COLLEGE WORK

Years Attended		Institution	Major and Minor	Degree	Experience Credits See reverse side
From	To				
Total Education Experience Credits					

RECORD OF QUALIFYING EXPERIENCE IN PLASTICS

Dates				Give your title, name and location of employer, and name of immediate superior for each position. List in chronological order. Describe duties fully and state briefly any important engineering work you have done in in each position. If space is not sufficient, use a separate sheet.	Time in years and months
From		To			
Mo.	Yr.	Mo.	Yr.		

I certify that the statements made in this application are correct. I agree, if elected, to be governed by the Constitution and By-Laws of the Society, and to promote the objective of the Society.

Total qualifying years of experience.

Total education and qualifying experience credits.

NATIONAL CREDENTIALS COMMITTEE USE ONLY

Approved (Signature)

Date _____

Approved (Signature)

Date _____

Date of Application

Signature in ink.

COMPLETING THE APPLICATION

Grade of Membership . . .

Membership grades are based on experience credits which are earned as follows:

1. Experience credits earned for education.

- Doctorate in science or engineering subject: **6 credits**
- Masters in science or engineering subject: **5 credits**
- Bachelors in science or engineering subject: **4 credits**
- Other degree in non-science or non-engineering subject: **2 credits**

Maximum credits allowable for education shall be six (6).

When filling in the "Statement of College Work" on the reverse side of this application, please place the corresponding number of credits earned in the right-hand column.

2. Experience credits for qualifying experience in plastics or plastics engineering are earned at the rate of one (1) per year, e.g. 5½ years of qualifying experience = 5½ credits. Please detail carefully the engineering skill required for each position to help the Credentials Committee judge experience as "qualifying."

When filling in the "Record of Qualifying Experience in Plastics" on the reverse side, please place the amount of time spent in each position (in years and months) in the right-hand column.

When you have determined the number of credits which you believe you have earned consult the following membership grade requirements. Indicate on the reverse side the grade of membership for which you believe you are qualified.

GRADE	REQUIREMENTS
Senior Member	Minimum of twelve (12) experience credits and maintained continuous membership in the Society for a minimum of two (2) years.
Member	Minimum of six (6) experience credits
Affiliate Member	Less than six (6) experience credits
Student Member	Regularly enrolled student (full- or part-time) in a course of study in plastics and between the ages of 16 years and 26 years, inclusive.

THIS PORTION MUST BE COMPLETED FOR PROCESSING OF YOUR APPLICATION.

Please check off the principal activity of your company under either Manufacturing or Non-Manufacturing.

MANUFACTURING.

- 1. ☐ Electrical & Electronic Machinery, Equipment & Appliances
- 2. ☐ Motor Vehicles and Equipment
- 3. ☐ Transportation Equipment (except Motor Vehicles)
- 4. ☐ Professional, Scientific and Controlling Instruments, Photographic & Optical Goods, Clocks
- 5. ☐ Iron, Steel, & Nonferrous Metals & Machinery (except Plastic & Electrical Machinery)
- 6. ☐ Fabricated Metal Products and Housewares
- 7. ☐ Finished Apparel Products
- 8. ☐ Food and Tobacco Products
- 9. ☐ Toilet Preparations, Drugs and Insecticides
- 10. ☐ Paints, Varnishes, and Industrial Chemicals (except Plastic Raw Materials)
- 11. ☐ Petroleum, Coal, Rubber, Stone and Glass Products
- 12. ☐ Musical Instruments, Toys, Sporting Goods, Athletic Goods, Ordnance & Smokers' Supplies
- 13. ☐ Jewelry and Fashion Accessories
- 14. ☐ Furniture and Finished Wood Products
- 15. ☐ Leather and Leather Products
- 16. ☐ MANUFACTURING, other than above. Please specify _____

- 17. ☐ Plastics Custom Molders, Extruders, Laminators, and Fabricators
- 18. ☐ Plastic Materials
- 19. ☐ Producers and Processors of Textiles, Lumber, Paper, Oils, Dyes, Chemicals, etc. used in Manufacture of Plastics
- 20. ☐ Plastic Machinery

NON-MANUFACTURING

- 21. ☐ Government: Federal, State, Municipal and Foreign; Officers of the Armed Forces
- 22. ☐ Advertising Agencies, Sales Consultants and Sales Engineers
- 23. ☐ Libraries, Schools, Colleges and Trade Associations
- 24. ☐ Consultants and Research Organizations, Architects, Engineers, Designers, Chemists
- 25. ☐ Transportation Operating Companies
- 26. ☐ Retail Stores
- 27. ☐ Exporters, Importers, Distributors, Jobbers, Wholesalers and Manufacturers' Agents
- 28. ☐ Doctors, Lawyers and other Professionals
- 29. ☐ NON-MANUFACTURING, other than above. Please specify _____
- 30. ☐ Packaging & Containers
- 31. ☐ Aerospace
- 32. ☐ Construction Materials



MEMBERSHIP APPLICATION

SOCIETY OF PLASTICS ENGINEERS, INC.
656 West Putnam Avenue
Greenwich, Connecticut 06830

SPE SECTIONS

AKRON	NORTHERN INDIANA
ARIZONA	NORTHWEST
BALTIMORE	PENNSYLVANIA
WASHINGTON	OMAHA
BARTLESVILLE/TULSA	ONTARIO
BINGHAMTON	PACIFIC NORTHWEST
BUFFALO	PALISADES
CENTRAL INDIANA	PHILADELPHIA
CENTRAL NEW YORK	PIONEER VALLEY
CENTRAL OHIO	PITTSBURGH
CHICAGO	QUEBEC
CLEVELAND	ROCHESTER
CONNECTICUT	ROCK VALLEY
DELAWARE VALLEY	ROCKY MOUNTAIN
DETROIT	ST. LOUIS
EAST CENTRAL	SOUTH TEXAS
ILLINOIS	SOUTHEASTERN OHIO
EASTERN NEW ENGLAND	SOUTHERN
FLORIDA	SOUTHERN CALIFORNIA
GOLDEN GATE	SOUTHEASTERN NEW ENGLAND
HUDSON-MOHAWK	SOUTHWEST VIRGINIA
JAPAN	TENNESSEE VALLEY
KANSAS CITY	TOLEDO
KENTUCKIANA	TRI STATE
MIAMI VALLEY	UPPER MIDWEST
MID-MICHIGAN	VIRGINIA-CAROLINA
MILWAUKEE	WESTERN MICHIGAN
MONTERREY	WESTERN NEW ENGLAND
NEW YORK	NON-SECTION
NEWARK	
NORTH TEXAS	